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STUDIES

FROM THE

CHEMICAL LABORATORY OF THE SHEFFIELD SCIENTIFIC SCHOOL

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This series of volumes is respectfully dedicated to

The Graduates of the University

STUDIES

FROM THE

CHEMICAL LABORATORY

OF THE

SHEFFIELD SCIENTIFIC SCHOOL

EDITED BY

HORACE L. WELLS

Professor of Analytical Chemistry and Metallurgy

VOLUME I.

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PREFACE

THE object of this publication is to show what the Sheffield Chemical Laboratory has done and is doing in the way of scientific research, and to bring together some of the more recent papers in several lines of work in a form convenient for study and reference. A bibliography is given which shows the work of the present officials during their connection with the laboratory, while a selection of articles that have been published during the past ten years, or are soon to appear, forms the main part of the book. A brief historical sketch of the laboratory is also presented.

H. L. W.

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SHEFFIELD LABORATORY.

THE Chemical Department of the Sheffield Scientific School holds the distinction of having been the starting-point of the school. The Philosophical Department of Yale College, as it was at first called, formed its first class in 1847, using as a laboratory the old President's House, which stood on the College Campus where Farnam Hall now stands. John P. Norton, Professor of Agricultural Chemistry, and Benjamin Silliman, Jr., Professor of Applied Chemistry, were the first instructors; and among the earliest students were G. J. Brush, W. H. Brewer, and S. W. Johnson, who have been so prominent in the development of the school.

Yale College had taken an early prominence in chemistry from the fact that Benjamin Silliman, the elder, had begun his labors here in 1804. He had just returned from England, where he had pursued chemical studies and had attended lectures by John Dalton, the founder of the atomic theory. In 1818 he founded the "American Journal of Science," which has been published continuously to the present time, and is one of the oldest scientific periodicals in the world. Most of the publications from the Sheffield Laboratory until recent times have appeared in this journal.

The chemical laboratory in the old President's House continued to be used for a period of thirteen years. Meanwhile Professor Silliman, the younger, had severed his active connection with it, and Professor Norton, after a highly valued service of five years, had died at the early age of thirty, and was succeeded by Professor John A. Porter.

Through the liberality of Joseph E. Sheffield the Chemical Department, now united to an Engineering Department which had existed on the College ground for a number of years, was removed in 1860 to the building now known as Sheffield

Hall. Here laboratories which were very commodious and complete for their day were fitted up, and the Sheffield Chemical Laboratory, gradually expanding as other departments were provided with new buildings, remained in this place for a period of thirty-five years.

Professor Brush had been appointed to the chair of Metallurgy in 1855, and S. W. Johnson became Professor of Analytical Chemistry in 1856, while the laboratory was still in the old President's House. The entire charge of the laboratory was soon put into the hands of these two gentlemen. Professor Porter, who was Mr. Sheffield's son-in-law, resigned in 1864 on account of ill-health, and died two years later.

The history of the laboratory in Sheffield Hall was one of steady growth and development; a wider range of instruction was gradually introduced, and from it have branched the departments of Mineralogy and Physiological Chemistry. Professor Brush at an early date turned his attention to mineralogy, which he taught for many years, and in which he made many important investigations, an account of which appears in another volume of this series. He gradually gave up his direct connection with the Chemical Department on account of his duties as executive officer of the school.

Professor R. H. Chittenden began instruction in physiological chemistry in 1875. From his efforts grew the Department of Physiological Chemistry and Physiology, which for a time was housed in Sheffield Hall with the chemical laboratory, until in 1889 the acquisition of the Sheffield Mansion gave it independent quarters.

Professor Johnson paid particular attention to agricultural chemistry, in which he became a leading authority, and continued to teach this subject, as well as organic and theoretical chemistry, until his retirement as Professor Emeritus in 1895.

From 1871 to 1886 Professor O. D. Allen took charge of the instruction in analytical chemistry and metallurgy. His work with Professor Johnson on cæsium compounds and in correcting Bunsen's first determination of the atomic weight

of cæsium was very important. Professor Allen was obliged to retire from the school in 1886 on account of poor health.

Professor Brewer, who was appointed to the chair of Agriculture at an early date, took charge of the instruction in elementary chemistry for a number of years. Since 1874 this instruction has been in charge of Professor W. G. Mixter, who has also carried out many investigations, particularly in the lines of organic and physical chemistry.

In 1895 the Chemical Department moved from Sheffield Hall into a new laboratory, which now affords the space and facilities required by its growth. This building, which is wholly devoted to chemistry, is one hundred and twenty-nine feet long, seventy-three feet wide in front, and sixty-three feet wide in the rear, and has three stories with a high basement. The laboratory is finely equipped for work in elementary, analytical, organic, inorganic, and physical chemistry, and contains a large chemical library.

The present chemical force consists of Professor Mixter, who has been mentioned previously; the writer, who was appointed as instructor in 1884, and has had charge of the analytical chemistry and metallurgy since Professor Allen's retirement; Assistant Professor H. L. Wheeler, who has under his care most of the investigations in organic chemistry; Mr. W. J. Comstock, who gives the greater part of the class-room instruction in organic chemistry; Assistant Professor P. T. Walden, who is associated with Professor Mixter in the work of instruction in elementary chemistry; Dr. James Locke, instructor in inorganic chemistry; Dr. Bayard Barnes, instructor in organic chemistry; and Dr. H. W. Foote, instructor in physical chemistry.

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On the Cæsium Antimonious Fluorides and some other Double Halides of Antimony, by H. L. Wells and F. J. Metzger.*

On the Separation of Tungstic and Silicic Acids, by H. L. Wells and F. J. Metzger.*

On a Salt of Quadrivalent Antimony, by H. L. Wells and F. J. Metzger.*

On the Purification of Cæsium Material, by H. L. Wells.*

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On Cæsium Periodate and Iodate-Periodate, by H. L. Wells.*

On the Double Chlorides of Cæsium and Thorium, by H. L. Wells and J. M. Willis.*

On a Cæsium Tellurium Fluoride, by H. L. Wells and J. M. Willis.*

On the Periodic System and the Properties of Inorganic Compounds: II. Gradations in the Properties of Alums, by James Locke.*

On the Periodic System and the Properties of Inorganic Compounds: III. The Solubilities of Alums as a Function of Two Variables, by James Locke.*

Generalizations on Double Halogen Salts, by H. L. Wells.*

* To be published.

PAPERS ON
GENERAL INORGANIC CHEMISTRY

ON A SERIES OF CÆSIUM TRIHALIDES.*

By H. L. WELLS.

INCLUDING THEIR CRYSTALLOGRAPHY.

By S. L. PENFIELD.

In the course of some experiments with cæsium compounds, bromine was added to a concentrated solution of cæsium chloride with an astonishing result. There was instantly formed a bright yellow precipitate, so dense as to nearly solidify the liquid. The substance readily dissolved on warming the liquid, and, on cooling it, large crystals of a yellowish-red color were formed which were found to be $CsClBr_2$.

In view of the fact that KI_3 was already known,† this discovery made it probable that a series of cæsium trihalides could be obtained. An attempt was accordingly made to prepare each of the following possible members of such a series containing chlorine, bromine, and iodine.

1. CsI_3	6. $CsCl_2I$
2. $CsBrI_2$	7. $CsBr_3$
3. $CsBr_2I$	8. $CsClBr_2$
4. $[CsClI_2$	9. $CsCl_2Br$
5. $CsClBrI$	10. $[CsCl_3]$

As a result, all the members of the series except the two enclosed in brackets were isolated.

These eight trihalides are easily made, being much less soluble than the normal halides. They crystallize beautifully, have remarkably brilliant colors, and some of them possess an unexpected degree of stability.

* Amer. Jour. Sci., xliii, January, 1892.

† Jörgensen, J. pr. Ch., II, ii, 357; Johnson, J. Chem. Soc., 1877, 249.

Method of Preparation.

Each of these compounds can be made by dissolving, with the aid of heat, the appropriate normal cæsium halide and the halogen or halogens indicated by the formula in the proper amount of water, or, in the single case of $CsBrI_2$, in weak alcohol, and cooling to crystallization. The cæsium salt used in making the mixed trihalides is preferably the one which is not decomposed by the halogen or halogens added. In most cases the presence of an excess of the normal halide is desirable in order that the halogens, especially iodine, may readily dissolve and not separate again on cooling, but the same result may also be obtained by the use of weak alcohol. Details of preparation will be given for each body separately.

Color.

In the following list the compounds are arranged in order, from the darkest to the lightest. The colors given, unless otherwise specified, are for crystals of considerable size, for when the bodies are obtained as precipitates, or when the crystals are pulverized, they are lighter in color.

CsI_3	Brilliant black, nearly opaque; powder brown.
$CsBrI_2$	Dark reddish-brown; thin crystals transmit deep red light; powder dark red.
$CsBr_2I$	Deep cherry-red.
$CsClBrI$, $CsBr_3$, $CsClBr_2$	Yellowish-red, each having a somewhat yellower tint than the one preceding it.
$CsCl_2I$	Orthorhombic variety, deep orange. Rhombohedral variety, pale orange.
$CsCl_2Br$	Bright yellow.

Stability on Exposure.

The five bodies containing iodine are much more stable than the others, and will bear long exposure to the air at ordinary temperatures with very slight superficial change. This exposure in some cases may be continued for a week or

more in warm weather without producing any marked alteration of color, but they constantly give off a slight odor and finally begin to whiten. The three compounds containing no iodine usually become white in a few hours on exposure, but even these can be preserved indefinitely in tightly corked tubes. Experiments showed that $CsBrI_2$ whitened more rapidly than $CsBr_2I$, also that $CsClBr_2$ decomposed more rapidly than $CsCl_2Br$. This indicates that their stability does not entirely depend upon the volatility of the halogens contained in them, — a point which has a bearing on the constitution of this group of bodies, and which will be considered subsequently.

Behavior when Heated.

The following table shows the temperatures of complete decomposition as determined by the change of color to white. They are only approximate, since they represent gradual changes which vary somewhat with the rapidity of heating. The melting-points are also given. In open tubes these are usually sharp, but in sealed tubes often very gradual.

	Melts in open tube. (uncorr.)	Melts in sealed tube. (uncorr.)	Becomes white in open tube. (approximate.)
CsI_3	210°	201°–208°	330°
$CsBr_2I$	246°	243°–248°	320°
$CsClBrI$	238°	225°–235°	290°
$CsCl_2I$	238°	225°–230°	290°
$CsBrI_2$	208°	155°–190°	260°
$CsBr_3$	whitens	180°	160°
$CsCl_2Br$	whitens	205°	150°
$CsClBr_2$	whitens	191°	150°

Behavior with Solvents.

All these bodies except $CsBrI_2$, which is almost completely decomposed by water, can be recrystallized by treating with warm water and cooling the solution. There is usually some decomposition during this operation, accompanied by the separation of iodine or the volatilization of this or the other halogens.

All the trihalides containing iodine can be dissolved in alcohol and recrystallized from it. There is usually a slight deposition of normal halide at the same time, which can be avoided by adding a little water to the alcohol. CsI_3 is much more soluble in alcohol than in water. The other iodine compounds, with the exception of $CsBrI_2$, which decomposes with water, are apparently more soluble in water. Those bodies containing no iodine are all decomposed by alcohol, leaving a white residue. Mixtures of alcohol and water are good solvents for all the trihalides.

Ether has no immediate action on the more stable compounds, CsI_3, $CsBr_2I$, $CsClBrI$, and $CsCl_2I$, but it decomposes all the others with separation of normal halides. When $CsBrI_2$ is thus decomposed, pure CsBr is left.

Crystallography.

The crystallization of the cæsium trihalides is orthorhombic. The salts form an isomorphous group, the chief features of which will first be given, followed by a brief description of the different individuals.

The forms which have been observed are:

a, 100, i-$\bar{i}$	*g*, 012, $\frac{1}{2}$-$\check{i}$
b, 010, i-$\check{i}$	*d*, 011, 1-$\check{i}$
c, 001, *O*	*f*, 021, 2-$\check{i}$
m, 110, *I*	*e*, 102, $\frac{1}{2}$-$\bar{i}$

Of these *m*, *d*, and *e* are the most prominent and usually determine the habit of the crystals. Either *m* or *d* usually predominates to such an extent that the crystals are prismatic in the direction of the vertical or the brachy-axes. The dome *f* is very common, but is usually too small to give a characteristic habit, and is therefore omitted from most of the figures. The face *g* was observed only on CsI_3. The pinacoids are variable in their development, but commonly one, and frequently all three, can be found on a single crystal. Pyramidal faces are practically wanting. In the examination of a great many crystals, but one was found (of $CsBr_2I$) on

which a single pyramidal face occurred; this replaced the edge between *m* and *d*, and had the symbol 132, $\frac{3}{2} - 3$. The cleavage is perfect, parallel to *c*.

An idea of the similarity of the different salts may be obtained from the following table, in which the axial ratios * and three of the prominent angles are given. The angles which were chosen as fundamental are marked by an asterisk, the others are calculated, and in all cases the measurements showed close agreement.

		I	II
		a : *b* : *c*	*a* : *b* : *c*
Series with iodine	CsI_3	0.6824 : 1 : 1.1051	1 : 1.4655 : 1.6196
	$CsBrI_2$	0.6916 : 1 : 1.1419	1 : 1.4460 : 1.6511
	$CsBr_2I$	0.7203 : 1 : 1.1667	1 : 1.3882 : 1.6196
	CsClBrI	0.7230 : 1 : 1.1760	1 : 1.3831 : 1.6268
	$CsCl_2I$	0.7373 : 1 : 1.1920	1 : 1.3563 : 1.6167
Series without iodine	$CsBr_3$	0.6873 : 1 : 1.0581	1 : 1.4550 : 1.5395
	$CsClBr_2$	0.699 : 1 : . . .	1 : 1.430 : . . .
	$CsCl_2Br$	0.7186 : 1 : 1.1237	1 : 1.3917 : 1.5638

	$m \wedge m$, 110 ∧ 1$\bar{1}$0	$d \wedge d$, 011 ∧ 0$\bar{1}$1.	$e \wedge e$, 102 ∧ $\bar{1}$02.
CsI_3	*68° 37′	*95° 43′	78° 0′
$CsBrI_2$	*69° 20′	97° 34′	*79° 5′
$CsBr_2I$	*71° 32′	*98° 48′	78° 0′
CsClBrI	*71° 44′	*99° 15′	78° 15′
$CsCl_2I$	72° 48′	*100° 1′	*77° 54′
$CsBr_3$	*69° 0′	*93° 14′	*75° 10′
$CsClBr_2$	*69° 56′		
$CsCl_2Br$	*71° 24′	*96° 40′	76° 0′

CsI_3 and $CsBr_3$ are almost identical in axial ratios, but it is surprising that the chemically intermediate compounds, $CsBrI_2$ and $CsBr_2I$, are not crystallographically intermediate.

A very remarkable relation exists between the first five compounds in the table, all of which contain iodine and are

* The ratios are given in two ways: I, with $\bar{b}$ as unity, as is customary; and II, with $\dot{a}$ as unity, in order to show more clearly the relation between $\dot{a}$ and $\dot{c}$.

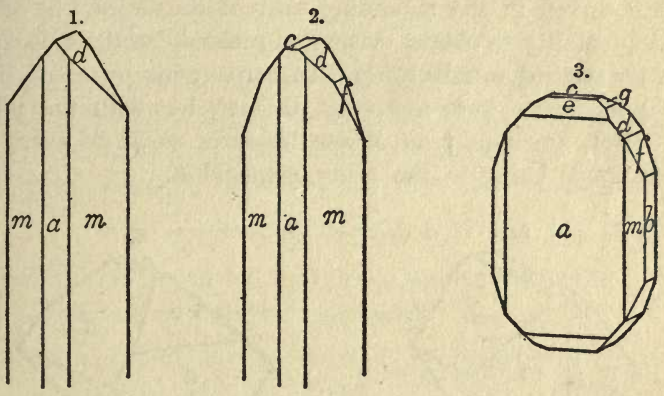
arranged in the order of their molecular weights. The ratio of two axes remains nearly constant throughout, while the third varies.* Exactly the same relation exists between the three compounds containing no iodine, but in this series the ratio between the two constant axes varies slightly from the corresponding ratio in the iodine compounds.

If an arrangement according to molecular weights is made with all the compounds containing bromine, or in like manner with all those containing chlorine, a symmetrical series of axial ratios is not formed. This leads to the conclusion that the two series given in the table have a special significance, and that iodine, with the highest atomic weight, plays an important part in the constitution of the first, while bromine acts in the same way in the second. Since several of the compounds contain only a single halogen atom of highest atomic weight, it follows that a single atom throughout exerts an influence on the symmetry of the series. This peculiar part played by an iodine or bromine atom may be explained by supposing it to be closely united either with the cæsium or with one of the other halogen atoms. It seems probable from these considerations that the three halogen atoms in these compounds do not have similar positions in the molecule, and consequently that the trihalides are not compounds of trivalent cæsium but have some other structure.

CsI_3. — Of this salt, crystals from both aqueous and alcoholic solutions were examined. On the former the forms *a*, *c*, *m*, *d*, and *f* were observed. The habit was different from anything else in the series, being needle-like, with *a* and *m* in the prismatic zone, terminated by *d*, Fig. 1, or by *c*, *d*, and *f*, Fig. 2. The crystals did not give very satisfactory reflections, but the best measurements, from a number of selected crystals, agreed closely with those given in the table. The crystals examined were 20–30 mm. in length and seldom over 2 mm. in diameter. On the crystals from alcohol, the forms *a*, *b*, *c*, *m*, *g*, *d*, *f*, and *e* were observed. The habit is shown in Fig. 3.

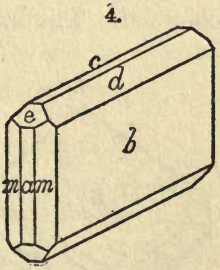
* Several series of organic compounds with analogous axial relations have been observed by Groth (Berichte, iii, 449) and by Hintze (Berichte, vi, 593).

There was a tendency in the crystals to arrange themselves in parallel position, forming plates showing large *a* faces, but the



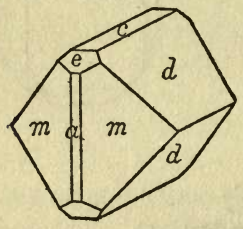
separate individuals were small, scarcely over 3 mm. in greatest diameter. The faces gave excellent reflections. The crystals are black, transmit a brownish-red light only on the thinnest edges, and are too opaque for optical examination.

CsBrI$_2$. — On two separate samples of this salt the forms *a*, *b*, *c*, *m*, *d*, *f*, and *e* were observed. The crystals are thin tables somewhat lengthened in the direction of the brachy-axis, Fig. 4. On examining the general table, it will be seen that this is the only one of the first five salts in which the angle $e \wedge e$ varies considerably from 78°. Here the variation amounts to a little over one degree, but in all probability this is not to be accounted for by imperfections in the crystals or inaccuracy in the observation, for from two different crops of crystals good reflections and almost identical measurements were obtained. The crystals were only a fraction of a millimetre in thickness, and not over 10 mm. long in the direction of the brachy-axis. With the polarizing microscope the tables show a decided pleochroism. For

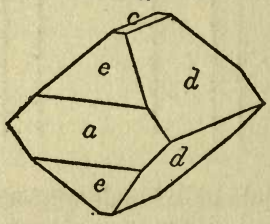


rays vibrating parallel to the $\dot{c}$ axis the color is dark brown, almost opaque, while for vibrations parallel to $\ddot{a}$ it is a rich reddish brown. A similar though less marked pleochroism was observed in the remaining salts of the series, but owing to the inability to obtain orientated pinacoid sections, it could not be studied satisfactorily. In convergent polarized light the phenomena were not very distinct, but with the tables of $CsBrI_2$ apparently an obtuse bisectrix could be seen, the optical axis being in the macro-pinacoid $\ddot{a}$.

5.



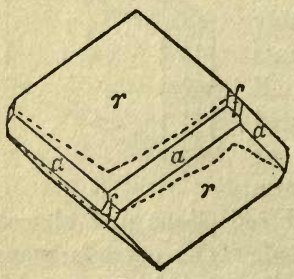
6.



$CsBr_2I$. — On this salt the forms *a*, *c*, *m*, *d*, *f*, and *e* were observed. The habit is shown in Fig. 5. The crystals were brilliant and gave excellent reflections. Those submitted for measurement were about 3 mm. in greatest diameter.

$CsClBrI$. — On this salt the forms *b*, *c*, *m*, *d*, *f*, and *e* were observed. The habit is like Fig. 5, but much longer, or prismatic, in the direction of the brachyaxis. The crystals were about 2 mm. in diameter and 10 in length.

7.



$CsCl_2I$. — This compound is dimorphous.

On the orthorhombic modification the forms *a*, *c*, *m*, *d*, *f*, and *e* were observed, but *m* and *f* are usually wanting. The habit is shown in Fig. 6. The crystals were about 2 mm. in diameter.

The hexagonal, rhombohedral variety occurred in curious saddle-shaped scales, with bright crystal faces only along

the edges. The forms which were observed are r (1, $10\bar{1}1$), f (−2, $02\bar{2}1$), and a (i-2, $11\bar{2}0$), Fig. 7. Only that portion is perfect which is included between the irregular dotted lines, the upper and lower angles of the rhombohedrons being truncated by irregular warped surfaces. In their growth the individuals of a whole series of crystals, with similar orientation, are piled upon one another in the direction of the vertical axis. The scales are about 6 mm. in diameter.

The measurement which was taken as fundamental is:

$$r \wedge r, \text{ over } a,\ 10\bar{1}1 \wedge 01\bar{1}\bar{1} = 99° 48'$$

giving for the length of the vertical axis, $c = 0.96363$. The following measurements were also made:

$a \wedge a = 60° 0', 60° 1', 59° 59'$	Calculated 60° 0′
$a \wedge f$, $\bar{1}2\bar{1}0 \wedge 02\bar{2}1 = 37° 45'$	" 37° 49′

The remaining compounds containing no iodine were much more unstable than those previously described. By making the measurements in a cold room very satisfactory results were obtained, the crystals retaining enough lustre to give good reflections, even after they had suffered considerable decomposition.

$CsBr_3$. — The forms observed on this salt are b, m, and d. The habit is short prismatic, with either m or d predominating, while b is usually wanting. Single crystals are sometimes 10 mm. in length, but groups of small crystals are more apt to occur.

$CsClBr_2$. — The only forms observed on this salt are m and c. The habit is short and stout prismatic. Single crystals are sometimes 15 mm. in length.

$CsCl_2Br$. — The forms observed on this salt are c, m, and d. It crystallized in stout prisms, over 10 mm. long, terminated like Fig. 1.

Method of Analysis.

The samples were prepared for analysis by pressing on paper. The drying was not always very good, both on

account of the haste sometimes necessary to avoid too much decomposition, and on account of the great tendency of the crystals to contain cavities filled with liquid.

Cæsium was invariably determined by weighing the normal halide produced by heating. In some cases where the resulting normal halide was slightly contaminated by a higher halogen, this was replaced by the proper one before weighing.

Where two halogens were present, they were determined in the usual way by weighing their silver salts and determining the loss in weight of these when heated in chlorine. In the cases where all three halogens were present, use was made of the extremely satisfactory method described by Gooch and Ensign.*

CsI_3.

This can be made by dissolving about one-fourth the theoretical amount of iodine in a solution of one part of cæsium iodide in ten parts of water. It generally gives a crop of brilliant, slender crystals. If a larger proportion of iodine is used, the substance generally separates in the form of crystalline plates without distinct faces. They are possibly a dimorphous form of the substance. If weak alcohol is used as a solvent instead of water, the theoretical amount of iodine can be taken and a well-crystallized product is obtained.

The following numbers show the composition:

	Found.		Calculated for
	Slender Crystals.	Plates.	CsI_3.
Cæsium	25.41	23.71	25.88
Iodine	72.67	. . .	74.12

When iodine is being dissolved in a warm aqueous solution of CsI, or when an attempt is made to dissolve CsI_3 in warm water, a heavy black liquid is formed at about 73° which solidifies on cooling to a crystalline mass. It is much richer in iodine than CsI_3 and probably contains a higher polyiodide. Analyses of the substance gave varying results, and although

* Amer. Jour. Sci., III, xl, 145, 1890.

most of these approached the composition CsI_5, it is still uncertain what body this is. The low melting-point of the substance is remarkable, since CsI_3 melts at 210° and iodine at 114°.

To find the solubility of CsI_3 in an aqueous solution of CsI, the mother-liquor from a crop of crystals deposited at about 20° was analyzed. It gave:

CsI 16.99 per cent.
I (free) 0.416 per cent or CsI_3 0.842 per cent.

The specific gravity of this mother-liquor was 1.154, hence 1 c. c. contained 0.0097gCsI_3. The body is so insoluble that, were we to use CsI in the place of KI in making a volumetric iodine solution, we could only obtain, at ordinary temperatures, a solution which would be about $\frac{1}{24}$ normal.

$CsBrI_2$.

Iodine dissolves in considerable quantity in a hot aqueous solution of cæsium bromide, but it nearly all separates on cooling. It is therefore necessary to use a mixture of alcohol and water in preparing this trihalide. A good crop of crystals was obtained by dissolving one-half the theoretical iodine in a solution of one part of cæsium bromide dissolved in two parts of water and one part (by volume) of alcohol.

The following numbers show the composition of the crystals:

	Found.	Calculated for $CsBrI_2$.
Cæsium	28.54	28.48
Bromine	18.11	17.13
Iodine	52.01	54.39

$CsBr_2I$.

This may be made by dissolving the theoretical amounts of iodine and bromine in a solution of one part of cæsium bromide in ten parts of water. A considerable excess of bromine does not interfere with its formation.

The crystals have the following composition:

	Found.	Calculated for $CsBr_2I$.
Cæsium	31.32	31.67
Bromine	37.63	38.09
Iodine	29.57	30.24

The solubility of this substance in water was approximately determined by estimating the free halogens volumetrically in the mother-liquor from a recrystallization at about 20°. The amount found corresponded to 4.45 per cent of $CsBr_2I$.

[*CsCl₂I.*]

Repeated attempts to make this substance, by using concentrated solutions of cæsium chloride and iodine in mixtures of water and alcohol and cooling to low temperatures, invariably failed.

CsClBrI.

This may be made by dissolving about one-fourth of the theoretical bromine and iodine in a solution of one part of cæsium chloride in five parts of water. If an excess of cæsium chloride is not taken, the product will contain too little chlorine and too much bromine.

An analysis of the product, properly prepared, gave:

	Found.	Calculated for CsClBrI.
Cæsium	34.24	35.42
Chlorine	9.36	9.45
Bromine	19.96	21.30
Iodine	32.36	33.83

If a large excess of bromine is used, an impure product results, as is shown by the following analysis of a sample thus made:

	Found.
Cæsium	36.11
Chlorine	9.36
Bromine	27.70
Iodine	24.83

On attempting to recrystallize the CsClBrI, a product of a darker red color is formed, sometimes accompanied by the

separation of some iodine. The following analyses were made of products of recrystallization:

"A" was from a single recrystallization. "B" was recrystallized three times, a little alcohol being added the last time to keep iodine in solution. "C" was recrystallized five times, each time with the addition of a large excess of bromine.

	A.	B.	C.	Calculated for $CsClBrI$.	Calculated for $CsBr_2I$.
Cæsium,	32.69	33.22	. . .	35.42	31.67
Chlorine,	3.32	5.02	2.70	9.45	0.
Bromine,	31.56	28.30	32.50	21.30	38.09
Iodine,	30.91	31.78	30.99	33.83	30.24

These analyses show that the recrystallized body approaches $CsBr_2I$, but that a part of the chlorine is very tenaciously held. The excess of bromine used in the case "C" had apparently no effect, probably because cæsium and iodine were present in equivalent quantities, whereas, in the case previously given, in which an excess of bromine was used in presence of much cæsium chloride in preparing the body, there was evidently a contamination with $CsClBr_2$.

$CsCl_2I$.

This body is dimorphous, the form apparently depending upon the presence or absence of a large excess of cæsium chloride in the solution from which it crystallizes.

The rhombohedral variety is usually obtained by adding iodine in the proportion of one atom to one molecule of cæsium chloride dissolved in about ten parts of water, then passing chlorine into the liquid, heated nearly to boiling, until the iodine just dissolves, and finally cooling. If an excess of chlorine is used, the body $CsCl_4I$ is formed, corresponding to KCl_4I discovered by Filhol.* This new cæsium compound will be described in a subsequent article in connection with several other new bodies of the same class.

The orthorhombic variety of $CsCl_2I$ can be obtained by using

* Michälis, Anorg Chem., iii, 102; Gmelin-Kraut, II, 1, 82.

three or four times as much cæsium chloride as in the other case, the other conditions remaining unchanged.

The following analyses of two separate products of each of the two varieties were made:

	Rhombohedral. Found.		Orthorhombic. Found.		Calculated for $CsCl_2I$.
Cæsium,	39.20	39.92	38.43	40.00	40.18
Chlorine,	20.72	21.08	19.78	20.75	21.45
Iodine,	37.81	38.21	38.97	38.88	38.37

On recrystallizing either form of this substance, from solution in hot water, the rhombohedral variety is usually formed, owing to the lack of an excess of cæsium chloride. It is not unusual, however, to obtain at first, as the solution cools, slender needles evidently of the orthorhombic variety, which afterward become surrounded by rhombohedral crystals.

$CsBr_3$.

To make this substance, one-half the calculated amount of bromine is added to a solution of one part of cæsium bromide in three parts of water, the whole is heated with vigorous shaking until the liquid bromine disappears, and then slowly cooled. Crystals gave on analysis:

	Found.	Calculated for $CsBr_3$.
Cæsium	35.12	35.66
Bromine	61.53	64.34

In preparing this body there usually remains, when the liquid bromine disappears on heating the solution, a heavy reddish liquid much lighter in color than bromine. It is without doubt a higher polybromide, and it probably corresponds to the easily fusible substance already mentioned as a probable higher polyiodide. An investigation of its composition will soon be made.

$CsClBr_2$.

The formation of this body was mentioned at the beginning of this article in connection with the discovery of the new

series of salts. It can be made by adding about one-half the theoretical bromine to a solution of cæsium chloride in about five parts of water, dissolving by heat and cooling.

The analyses of two products are given below. The "precipitate" resulted from adding bromine to a cold cæsium chloride solution, and, being finely divided as well as the most unstable compound of the series, it suffered a considerable amount of decomposition, although time was not taken to dry it thoroughly.

	Found.		Calculated for $CsClBr_2$.
	Precipitate.	Crystals.	
Cæsium,	40.62	42.14	40.49
Chlorine,	12.64	13.24	10.81
Bromine,	39.61	42.93	48.70
Water,	6.45	1.72	0.

$CsCl_2Br$.

This substance may be made by adding the calculated amount of bromine to a solution of cæsium chloride in five parts of water, warming enough to keep $CsClBr_2$ in solution, and passing chlorine in excess.

	Analysis gave	Calculated for $CsCl_2Br$.
Cæsium	46.25	46.83
Chlorine	24.15	25.00
Bromine	26.05	28.17

$CsCl_3$.

Efforts to prepare this substance by passing chlorine into saturated aqueous solutions of cæsium chloride, cooled by a freezing-mixture, did not succeed. It was noticeable that the compound $Cl.5H_2O$ was not formed under these circumstances.

Other Trihalides.

Johnson's KI_3* is undoubtedly analogous to the cæsium compounds. An investigation of this and other potassium

* J. Chem. Soc., 1877, i, 249.

trihalides, as well as the corresponding rubidium compounds, is now in progress in this laboratory, and an effort will be made to prepare similar compounds with still other metals.

The compound $KI_2(CN)$* and the body NH_4I_3, which Johnson describes† as very similar to KI_3, should be mentioned in this connection.

There have been described a great number of trihalides of both natural and artificial organic bases. These are mostly triiodides, but there are among them a number of tribromides and also mixed trihalides, especially of the type RCl_2I. These organic bodies‡ are evidently analogous to the cæsium compounds under consideration, but since they have not been sufficiently studied to throw any light on the structure or crystalline form of trihalides in general, they will not be mentioned in detail here.

Theoretical Considerations.

Thus far in this article, the simplest possible formulæ have been used. The probable structure of the compounds will now be discussed.

The trihalides previously known have been usually considered as weakly combined addition-products. Mendeléeff,§ for example, says that the instability with which I_2 unites with KI and $N(CH_3)_4I$ is analogous to the instability of many cryohydrates, e. g., $HCl.2H_2O$. It must be noticed that some of the cæsium trihalides are very stable, but this fact is evidently due to the strong positive character of the metal, and since others among them are comparatively unstable, it can have no important bearing on their structure.

Johnson‖ advances the formula K_2I_6 for potassium triiodide

* Langlois, Ann. Chim. Phys., [III] lx, 220. † J. Chem. Soc., 1878, 397.

‡ See the following articles: Weltzien, Ann. Ch. Ph., xci, 33; xcix, 1. Müller, ibid., cviii, 5. Hubner, ibid., ccx, 368. Ladenburg, ibid., ccxvii, 122. Zincke and Lawson, ibid., ccxl, 123. Zincke and Artzberger, ibid., ccxlix, 366. Jörgensen, J. pr. Ch., II, vols. ii, iii, xiv, and xv. Dafert, Monatshefte, iv, 496. Dittmar, Berichte, xviii, 1612. Ostermayer, ibid., xviii, 2298. Kamensky, ibid., xi, 1600. Tilden, J. Chem. Soc., xviii, 99. Hoogewerff and Dorp, Rec. Trav. Chim., iii, 361.

§ Grundlagen der Chemie, p. 563, foot-note 63.

‖ J. Chem. Soc., 1878, 183.

with no better reason than the existence of a higher iodide of mercury, HgI_6.* This formula may be dismissed at once, for there is no more ground for it than for writing K_2I_2 because HgI_2 exists, and moreover, if the cæsium salts were Cs_2X_6, we should expect to find in the series such compounds as Cs_2Cl_5I, $Cs_2Cl_3I_3$, etc., none of which were discovered.

Since the members of the cæsium series are crystallographically isomorphous, they must all have the same structure, and, as has just been shown, no multiple of the formula CsX_3 is probable.

A possible explanation of the cæsium trihalides may be made by supposing the metal to act trivalently, and the following arguments seem to favor this view:

1st. Cæsium has the highest atomic weight of the alkali-metals, and it is a noticeable fact that, among the elements in general, those with higher atomic-weights in a group have the greater tendency to act with variable quantivalence. 2d. Cæsium is univalent in its ordinary compounds, and, following the general rule, the next higher quantivalence should be three. 3d. Cæsium is in the same group as gold in Mendeléeff's periodic system of the elements, and it is well known that this element acts univalently and trivalently.

On the other hand, the following arguments are in favor of considering the bodies double salts: 1st. The compounds IBr, ICl, and BrCl are definite bodies; and all the trihalides may be considered as molecular compounds of these, and also the molecules I_2 and Br_2, with normal halides. 2d. The fact that $CsBr_2I$ is more stable than $CsBrI_2$, and that $CsCl_2Br$ is more so than $CsClBr_2$, showing that the stability of these bodies does not entirely depend upon the volatility of the halogens contained in them, indicates that the halogen atoms have much influence on each other, and that at least two of them are probably bound together. A consideration of the fact that $CsCl_2I$ is a very stable body, while $CsClI_2$ probably cannot be prepared, leads to the same conclusion. 3d. It has been pointed out by Godeffroy † that the simple salts of cæsium are as a rule

* Jörgensen, J. pr. Ch., II, ii, 357.

† Berichte, ix, 1365.

more soluble than the corresponding rubidium and potassium salts, while with the double salts the reverse is true. Work now in progress in this laboratory shows that the rubidium and potassium trihalides, as far as they have been investigated, increase in solubility towards potassium; hence, if the rule holds true, they must be double salts. 4th. The new salt CsI.AgI,* an undoubted double salt, shows a close relation to the trihalides in its system of crystallization, in the ratio of the two axes which alone were determined, and in its cleavage.† The salt KI.AgI‡ has been prepared, but it has not yet been procured in crystals fit for measurement. Work will be continued on this class of compounds.

The evidence which has just been given points strongly towards considering the trihalides as double salts. The considerations based on the axial relations of the crystals, which have been given in the crystallographic part of this article, also indicate that these bodies cannot be viewed as compounds of trivalent cæsium, and, moreover, that a single halogen atom of highest atomic weight plays an important part in their structure. One view of the possible position of this peculiar atom may be that it is a trivalent atom united to the others in the manner indicated by the general formulæ $Cs-I<\overset{X}{X}$ and

* This was made by dissolving AgI in a concentrated, hot solution of CsI and cooling. It forms tufts of hair-like crystals, very seldom large enough to measure.

	Analysis gave	Calculated for CsI.AgI.
Silver	19.03	21.82
Iodine	50.91	51.32
Cæsium	...	26.86

† CsI.AgI crystallizes in the orthorhombic system. It was obtained in long needles, not over $\frac{1}{8}$ mm. in diameter and too small to show distinct end faces. A pinacoid and two other forms occur in the prismatic zone which correspond to $c(001)$, $g(012)$, and $d(011)$ of the trihalide series. Of these c and g are the best developed, while d is very small. Five independent measurements of $c \wedge g$ gave values varying between 27° 29′ and 27° 44′, the average being 27° 36′, which gives the ratio $\bar{b} : \dot{c} = 1 : 1.0456$. The crystals show an imperfect cleavage parallel to $a(100)$ and probably a second parallel to c, but they were too small to allow of this being determined with certainty. Under the polarizing microscope they show parallel extinction.

‡ Boullay, Ann. Chim. Phys., II, xxxiv, 377.

$Cs-Br<^{X}_{X}$. This view may be objected to because the strongest halogen atom is not directly united to the cæsium. The structure $Cs-X<^{X}_{\|X}$ is scarcely admissible in the compound CsI.AgI on account of the probable invariable univalence of silver.

Another view of the position of the peculiar iodine or bromine atom may be based upon the idea, so ably advocated by Remsen,* that a bivalent group of two halogen atoms acts the same part in double halides that oxygen takes in ordinary oxygen salts. Supposing that a halogen atom of highest atomic weight is linked to the cæsium atom by means of the other two halogen atoms, acting as a bivalent group, the trihalides have the following formulæ: —

Cs—(II)—I	Cs—(BrBr)—Br
Cs—(BrI)—I	Cs—(ClBr)—Br
Cs—(BrBr)—I	Cs—(ClCl)—Br
Cs—(ClBr)—I	
Cs—(ClCl)—I	
[Cs—(ClI)—I]	[Cs—(ClCl)—Cl]

These formulæ allow the supposition that the most negative halogen atom is in direct union with the cæsium. They are consistent with the view that there are two symmetrical series of compounds, one with an iodine atom, the other with a bromine atom in a special position. On these grounds they seem quite plausible.

Assuming that the structure of the trihalides is represented by the above formulæ, a comparison of their relative stability leads to the view that the linking group of two halogen atoms causes greater stability when composed of like atoms than when these atoms differ. The groups (II) (BrBr) and (ClCl) occur in the comparatively stable compounds, while (ClBr) is in the most unstable body of the "bromine series," (BrI) is in

* On the Nature and Structure of Double Halides, Amer. Chem. Jour., xi, 291.

the least stable one of the "iodine series," and the compound which should contain (ClI), with the least closely related halogens, could not be prepared. There is a possible exception in the body Cs—(ClBr)—I, for it has not been noticed that the stability of this varies to any marked extent from Cs—(ClCl)—I. The same view of the effect of the identity of the linking halogen atoms will probably apply to all double halides, for it is certain that very few of these containing different halogens are known, although this may be partly due to the fact that mixed double halides have not been sufficiently studied. An investigation of the double halides of cæsium and mercury, now in progress, indicates that the generalization will apply in this case. Whatever may be the true structure of double halides, this influence of the identity of the halogens in the combining simple salts probably depends upon the same broad chemical law which causes, for example, two oxides or two sulphides to combine more readily than an oxide and a sulphide of the same elements, and which causes sulphates to combine with other sulphates more readily than they combine with nitrates and other dissimilar salts.

The present communication may be considered as preliminary to a wider study of polyhalides and double halogen salts. It is hoped that other series, studied chemically and crystallographically, may give valuable results.

SHEFFIELD SCIENTIFIC SCHOOL,
December, 1891.

ON THE RUBIDIUM AND POTASSIUM TRIHALIDES.*

By H. L. WELLS and H. L. WHEELER.

WITH THEIR CRYSTALLOGRAPHY.

By S. L. PENFIELD.

The discovery of a series of cæsium trihalides † has led the writers to investigate the analogous rubidium and potassium compounds. The following table gives a list of the bodies which we have been able to prepare, together with the cæsium series for comparison. The compound $KI.I_2$ had been previously prepared by Johnson.‡

$CsI.I_2$	$RbI.I_2$	$KI.I_2$
$CsBr.I_2$	. . . . .	. . . . .
CsBr.BrI	RbBr.BrI	KBr.BrI
CsCl.BrI	RbCl.BrI	. . . . .
CsCl.ClI	RbCl.ClI	KCl.ClI
$CsBr.Br_2$	$RbBr.Br_2$	. . . . .
$CsCl.Br_2$	$RbCl.Br_2$	. . . . .
CsCl.ClBr	RbCl.ClBr	. . . . .

It is to be noticed that there is but one member lacking in the rubidium series to make it as complete as that of cæsium. We have repeatedly tried to prepare this compound, $RbBr.I_2$, using alcoholic solutions of varying strength and great concentration at low temperatures, but with no success. The failure to make this body doubtless depends upon the comparative instability of the rubidium series. We have even attempted to prepare $RbCl.I_2$ and $RbCl.Cl_2$, corresponding

* Amer. Jour. Sci., xliv, July, 1892.
† Ibid., III, xliii, 17.
‡ J. Chem. Soc., 1877, 241.

to which no cæsium compounds could be made, but, as was anticipated, these efforts were entirely without success.

In the potassium series, only those bodies could be prepared which correspond to the more stable cæsium and rubidium compounds. They show a great decrease in stability in comparison with the rubidium compounds. A product was obtained at a very low temperature, which was probably KBr. Br_2, but we did not make a satisfactory analysis of it.

We have attempted to prepare a number of sodium and lithium trihalides. There is no doubt that some of them exist, but they are so extremely soluble and unstable that we have abandoned work in this direction.

Method of Preparation. — The rubidium and potassium compounds are made, like the cæsium series, by dissolving a normal halide with the proper halogen or halogens in water with the aid of heat and cooling to crystallization. The members of the rubidium series, being very soluble, require very concentrated solutions for their preparation. The potassium compounds, being still more soluble, require the greatest possible degree of concentration, and are usually best obtained by exposing the solutions for a considerable time to a winter temperature, evaporation in the desiccator being sometimes also necessary.

Color. — The colors of the rubidium and potassium compounds are very similar to those of the corresponding members of the cæsium series, but, since they usually form larger crystals, their apparent color is generally somewhat darker. They vary in color from brilliant black in $RbI.I_2$ and $KI.I_2$, through various shades of yellowish-red and orange to bright yellow in the compound RbCl.ClBr. In all the compounds that have been prepared, the color becomes lighter as the sum of the atomic weights of the three halogen atoms decreases.

Stability. — It has been found by experiment that the potassium trihalides are much less stable on exposure to the air than the corresponding rubidium compounds, while these in turn are less stable than the members of the cæsium series. The same relative stability of the three series is shown by the

temperatures at which they are completely decomposed by rapid heating as given below:

Approximate Temperature of Whitening.

$CsI.I_2$, 330°	$RbI.I_2$, 270°	$KI.I_2$, 225°
CsBr.BrI, 320°	RbBr.BrI, 265°	KBr.BrI, 180°
CsCl.ClI, 290°	RbCl.ClI, 265°	KCl.ClI, 215°
CsCl.BrI, 290°	RbCl.BrI, 200°	. . . . .
$CsBr.Br_2$, 160°	$RbBr.Br_2$, 140°	. . . . .
CsCl.ClBr, 150°	RbCl.ClBr, 110°	. . . . .
$CsCl.Br_2$, 150°	$RbCl.Br_2$, 80°	. . . . .

Fusibility. — The melting-points of the analogous compounds become lower from cæsium to potassium. In the open capillary tube $RbI.I_2$ melts at 194° and RbCl.ClI at 208°, while all the other rubidium compounds whiten without melting. The potassium compounds give practically the same melting-points in open as in sealed tubes. The following table gives the approximate melting-points in sealed tubes:

$CsI.I_2$, 201°–208°	$RbI.I_2$, 190°	$KI.I_2$, 38°*
CsBr.BrI, 243°–248°	RbBr.BrI, 225°	KBr.BrI, 60°
CsCl.ClI, 225°–230°	RbCl.ClI, 180°–200°	KCl.ClI, 60°
CsCl.BrI, 225°–235	RbCl.BrI, 205°	. . . . .
$CsBr.Br_2$, 180°	$RbBr.Br_2$, whitens	. . . . .
CsCl.ClBr, 205°	RbCl.ClBr, whitens	. . . . .
$CsCl.Br_2$, 191°	$RbCl.Br_2$, 76°?	. . . . .

Behavior with Solvents. — The extreme solubility of the rubidium and potassium trihalides in water has already been referred to, and it has been pointed out that the members of the potassium series are the most soluble. The rubidium compounds which contain iodine can be recrystallized from water without difficulty. These four bodies containing rubidium and iodine are sufficiently stable to be soluble in alcohol, while the remaining rubidium compounds, as well as all the

* Johnson gives 45° for the melting-point of this compound (l. c.).

potassium compounds, are more or less readily decomposed by alcohol with the separation of normal halides. Ether decomposes all the rubidium and potassium compounds, leaving normal halides undissolved.

Crystallography.

The rubidium trihalides crystallize in the orthorhombic system and are isomorphous with the corresponding cæsium compounds, showing a close similarity both in crystalline habit and in axial ratios.

The forms which have been observed are:

a, 100, i-$\bar{i}$	*d*, 011, 1-$\breve{\imath}$
b, 010, i-$\breve{\imath}$	*f*, 021, 2-$\breve{\imath}$
c, 001, *O*	*e*, 102, $\frac{1}{2}$-$\bar{i}$
m, 110, *I*	*p*, 111, 1.

With the exception of the pyramid *p*, which was observed as a small face only on $RbI.I_2$, these are the same as were observed on the cæsium trihalides, while the brachydome *g*, 012, $\frac{1}{2}$-$\breve{\imath}$, which was found only on $CsI.I_2$, was not observed on any of the rubidium compounds.

Of the three potassium trihalides which were examined, only one, KBr.BrI, was orthorhombic like the cæsium and rubidium compounds. The others, $KI.I_2$ and KCl.ClI, are monoclinic, but they can be referred to axes which are similar to those of the orthorhombic series.

The cleavage of the rubidium trihalides is perfect parallel to *c*, less perfect parallel to *a;* neither is easily produced. The crystals are very brittle and usually break with a conchoidal fracture. The potassium trihalides are exceedingly brittle, and no cleavage was observed. The optical properties were not studied, owing to the difficulty of preparing orientated sections.

In the following table the axial ratios of all the alkali-metal trihalides are given, arranged as in the cæsium paper. In the table of angles those which were chosen as fundamental are marked by an asterisk.

	I. $a : b : c$	II. $a : b : c$
	Series with iodine.	
$CsI.I_2$	0.6824 : 1 : 1.1051	1 : 1.4655 : 1.6196
$RbI.I_2$	0.6858 : 1 : 1.1234	1 : 1.4582 : 1.6381
$KI.I_2$	0.7065 : 1 : . . .	1 : 1.4154
	Monoclinic, $a = 86° 47½'$	$a = 86° 47½'$
$CsBr.I_2$	0.6916 : 1 : 1.1419	1 : 1.4460 : 1.6511
$CsBr.BrI$	0.7203 : 1 : 1.1667	1 : 1.3882 : 1.6196
$RbBr.BrI$	0.7130 : 1 : 1.1640	1 : 1.4025 : 1.6325
$KBr.BrI$	0.7158 : 1 : 1.1691	1 : 1.3970 : 1.6333
$CsCl.BrI$	0.7230 : 1 : 1.1760	1 : 1.3831 : 1.6268
$RbCl.BrI$	0.7271 : 1 : 1.1745	1 : 1.3753 : 1.6153
$CsCl.ClI$	0.7373 : 1 : 1.1920	1 : 1.3563 : 1.6167
$RbCl.ClI$	0.7341 : 1 : 1.1963	1 : 1.3622 : 1.6296
$KCl.ClI$	0.7335 : 1 : 1.2204	1 : 1.3633 : 1.6638
	Monoclinic, $a = 83° 20'$	$a = 83° 20'$
	Series without iodine.	
$CsBr.Br_2$	0.6873 : 1 : 1.0581	1 : 1.4550 : 1.5395
$RbBr.Br_2$	0.6952 : 1 : 1.1139	1 : 1.4384 : 1.6023
$CsCl.Br_2$	0.699 : 1 : . . .	1 : 1.430 : . . .
$RbCl.Br_2$	0.70 : 1 : 1.1269	1 : 1.43 : 1.61
$CsCl.ClBr$	0.7186 : 1 : 1.1237	1 : 1.3917 : 1.5638
$RbCl.ClBr$	0.7146 : 1 : 1.1430	1 : 1.3994 : 1.5995

	$m \wedge m$, 110 ∧ $1\bar{1}0$	$d \wedge d$, 011 ∧ $0\bar{1}1$	$e \wedge e$, 102 ∧ $\bar{1}02$
$RbI.I_2$	*68° 53′	*96° 39′	78° 38′
$KI.I_2$	*70° 34′		
$RbBr.BrI$	70° 58′	*98° 40′	*78° 27′
$KBr.BrI$	71° 12′	*98° 55′	78° 28′
$RbCl.BrI$	72° 2′	*99° 10½′	*77° 51′
$RbCl.ClI$	72° 34′	*100° 13′	*78° 21′
$KCl.ClI$	72° 54′		*79° 8′
$RbBr.Br_2$	*69° 37′	*96° 10′	77° 24′
$RbCl.Br_2$	*70 approx.	*96° 58′	76° approx.
$RbCl.ClBr$	71° 6′	*97° 38′	*77° 18′

A comparison of the axial ratios of the trihalides shows that the replacement of cæsium by rubidium, and in one case

by potassium, has little or no effect on the form, while in two of the compounds potassium causes a change in symmetry without much change in the axes. It is evident that the rubidium salts, like those of cæsium, may be arranged in two symmetrical series, one with and the other without iodine, in which the ratio of two axes remains nearly constant throughout, while the third varies, and the conclusions which were arrived at in our previous paper concerning the constitution of the cæsium trihalides are confirmed by the rubidium compounds.

The rubidium trihalides have a strong tendency to crystallize, and the solubility is such that, from solutions of not over 50 c. c. in volume, large and magnificent crystals several centimetres in length, can readily be obtained. The size of the crystals seems often dependent only upon the volume of the solution and the size of the vessel containing it. Many of the large crystals are complex, being built up of smaller ones in parallel position. Some of the crystallizations were as beautiful as any that we have ever seen.

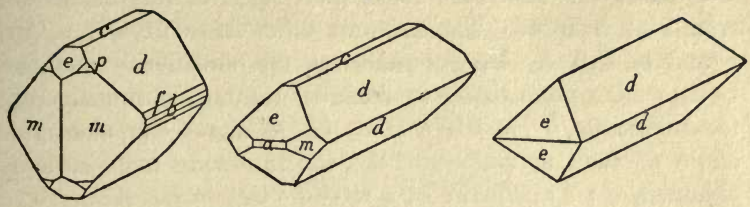
The rubidium trihalides containing iodine were measured at ordinary temperatures; those without iodine and the potassium trihalides at about 0° C. It was found that the stability of the compounds increased very rapidly with a diminution in temperature and, by working in the cold, no difficulty was experienced in making accurate measurements of the more unstable salts. It is not considered necessary to give with each trihalide a table of measured and calculated angles, but in all cases where a series of accurate measurements were obtained, they agreed closely with the calculated.

RbI.I$_2$. — The forms *b*, *c*, *m*, *d*, *f*, *e*, and *p* were observed. Of these *f* and *p* were always small and frequently wanting. The habit is shown in Fig. 1.

RbBr.BrI. — The forms of *a*, *c*, *m*, *d*, and *e* were observed. The habit is shown in Fig. 2.

RbCl.BrI. — The forms *a*, *d*, and *e* were observed. The pinacoid *a* is usually wanting, and the simple habit shown in Fig. 3 prevails.

1. 2. 3.

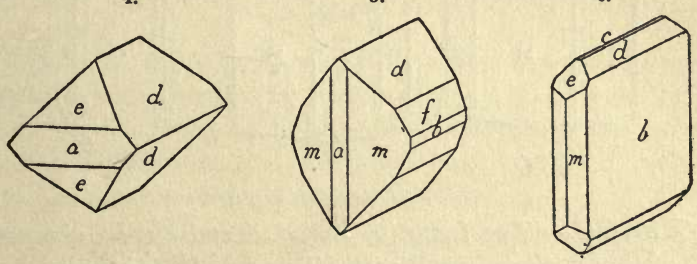


RbCl.ClI. — The forms *a*, *d*, and *e* were observed. The habit is shown in Fig. 4.

RbBr.Br$_2$. — The forms *a*, *b*, *m*, *d*, and *f* were observed. The habit is shown in Fig. 5.

RbCl.Br$_2$. — The forms *b*, *c*, *m*, *d*, and *e* were observed. The habit is shown in Fig. 6. The tendency of this salt is to crystallize in small scales; it is also the most unstable of the rubidium series, so that we considered it fortunate that

4. 5. 6.

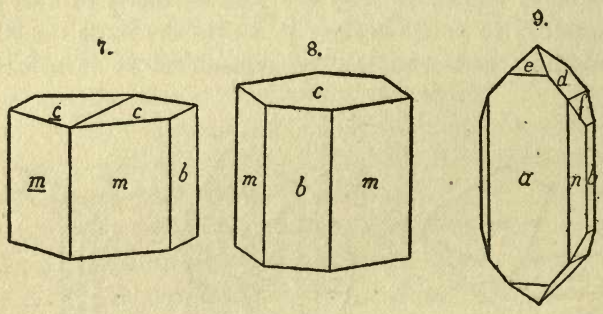


we were able to make out the axial ratio. The only faces which yielded good reflections were *b* and *d*, which established accurately the relation between the $\bar{b}$ and $\dot{c}$ axes, while only approximate measurements were obtained from the other faces.

RbCl.ClBr. — The forms *a*, *b*, *m*, *d*, and *e* were observed. The habit is like Fig. 2, except that *c* is wanting.

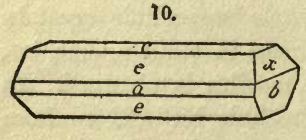
KI.I$_2$. — This occurs in very simple monoclinic crystals. If the solution is cooled slowly it forms in stout prisms, but by rapid cooling a network of fine needles is obtained. In order to make this salt and the monoclinic KCl.ClI conform to the position which has been adopted for the orthorhombic trihalides, it is necessary to deviate from the ordinary custom

and make the clino-axis slope from right to left instead of from back to front. The faces are taken as b, 010, $i\text{-}\bar{\imath}$; c, 001, O and m, 110, I. The crystals are not sufficiently modified to determine more than two axes, but taking as fundamental measurements, $b \wedge m$, $010 \wedge 110 = 54° 43'$ and $c \wedge c$ (re-entrant angle of twin crystal) $= 6° 25'$, the following axial ratio is obtained, $a : b = .7065 : 1$; $a = 0\bar{1}0 \wedge 001 = 86° 47\frac{1}{2}'$. The angle $m \wedge c$, $110 \wedge 001$, was measured 91° 55′ and 91° 50′, calculated 91° 51′. Fig. 7 represents a twin crystal in the above position. Fig. 8 represents a simple crystal in the ordinary monoclinic position, with $\dot{a}$ as the clino axis. The axial ratio for this position is, $\dot{a} : \bar{b} = 1.4154 : 1$; $\beta = 86° 47\frac{1}{2}'$.



KBr.BrI. — The forms a, b, n, d, f, and e were observed. The habit is shown in Fig. 9. This salt differs from all of the other alkali-metal trihalides in having the brachy prism n, 120, $i\text{-}\breve{2}$, instead of the unit prism m. The fundamental measurements were $a \wedge n$ $100 \wedge 120 = 55° 4'$ and $d \wedge d$, $011 \wedge 0\bar{1}1$, $= 98° 55'$.

KCl.ClI. — This crystallizes in long needles belonging to the monoclinic system, Fig. 10. Taking b as the clino axis, the forms are a, 100, $i\text{-}\dot{\imath}$; b, 010, $i\text{-}\bar{\imath}$; c, 001, O; x, 032, $\frac{3}{2}\text{-}\bar{\imath}$, and e, 102, $\frac{1}{2}\text{-}\dot{\imath}$. The measurements taken as fundamental are $c \wedge b$, $001 \wedge 010 = 96° 40'$, $e \wedge e$, $102 \wedge \bar{1}02 = 79° 8'$, and $c \wedge x$, $001 \wedge 032 = 66° 35'$, from



which the following axial ratio was calculated, $a : b : c = .7335 : 1 : 1.2204$, $a = 83° 20'$. If taken in the ordinary monoclinic position with e as the prism 110 and x as the orthodome $\bar{1}01$, the axial ratio from the above measurements becomes $\dot{a} : \dot{b} : \dot{c} = .8319 : 1 : .4544$; $\beta = 83° 20'$.

Method of Analysis.

The methods used for the analyses of the potassium and rubidium trihalides were exactly the same as those mentioned in the article on cæsium trihalides.

The crystals were prepared for analysis by pressing between papers and at the same time crushing them somewhat. In some cases, where the bodies were very easily decomposed, this was done in cold weather out of doors, but, even with this precaution, it was not possible to dry them very thoroughly or to avoid a considerable amount of decomposition.

$RbI.I_2$.

This body can be prepared by dissolving 55 g. of rubidium iodide in enough water to make a solution of 50 c. c., adding 60 g. of iodine, warming until solution takes place, and cooling to ordinary temperature. A mass of large crystals in parallel position, forming steps, is usually formed.

	Analysis gave		Calculated for $RbI.I_2$.
Rubidium	18.32	18.32	18.33
Iodine	81.07	. . .	81.67

A specific gravity determination, made in the mother-liquor at 22°, gave the number 4.03. This cannot be considered very exact, on account of the difficulty of obtaining the mother-liquor in such a condition that it neither dissolves nor deposits the substance. A sample of mother-liquor, of specific gravity 2.19, was found to contain 1.61 g. of $RbI.I_2$ in 1 c. c. The compound therefore dissolves in about one-third its weight of water at 22°. It is interesting to notice here that, under nearly the same conditions, the corresponding cæsium compound, $CsI.I_2$, requires more than one hundred parts of

water to dissolve it. It is expected that this great difference in solubility will form the basis of a useful method for separating the two metals.

RbBr.BrI.

This compound can be readily made by dissolving, with the aid of heat, 30 g. of iodine and 20 g. of bromine in a saturated aqueous solution of 40 g. of rubidium bromide and cooling. The facility with which this body crystallizes is remarkable. The large crystals have a color and lustre much like the mineral pyrargyrite, "ruby-silver."

	Analysis gave	Calculated for RbBr.BrI.
Rubidium	22.79	22.95
Bromine	45.19	42.95
Iodine	31.11	34.10

An approximate specific gravity determination, made with the mother-liquor, gave the number 3.84. An analysis of the mother-liquor showed that it contained about 44 per cent of RbBr.BrI. The mother-liquor of the corresponding cæsium compound contained only 4.45 per cent of CsBr.BrI.

RbCl.BrI.

This body can be made by adding 27 g. of bromine and 42 g. of iodine to a saturated aqueous solution of 40 g. of rubidium chloride, warming until all is in solution, and cooling. It forms magnificent crystals which can be readily recrystallized from water. Unlike the corresponding cæsium compound, it does not change its composition by recrystallization; hence it is probable that it is a true chemical compound, and not a mixture of the isomorphous bodies RbBr.BrI and RbCl.ClI.

	Analysis gave,		Calculated for RbCl.BrI.
	Original crystals.	6th recrystallization.	
Rubidium	26.67	27.34	26.06
Chlorine	10.65	. . .	10.82
Bromine	24.89	. . .	24.39
Iodine	38.13	. . .	38.72

RbCl.ClI.

A convenient method for preparing this compound is to pass chlorine into a warm, concentrated solution of rubidium chloride, containing the calculated amount of iodine, until the iodine is just dissolved. If too much chlorine is used, the compound $RbCl_4I$ is formed, which we shall describe in a future article. It is best to stop adding chlorine while the solution is still colored red by iodine. On cooling the liquid, the compound separates, usually in large flat groups of parallel crystals.

	Analysis gave	Calculated for RbCl.ClI.
Rubidium	29.85	30.15
Chlorine	24.68	25.04
Iodine	44.68	44.79

RbBr.Br$_2$.

This can be prepared by adding 49 g. of bromine to 45 c. c. of an aqueous solution containing 50 g. of rubidium bromide, warming gently until bromine dissolves, then cooling. It usually forms a mass of large, brilliant, red crystals in parallel position.

	Analysis gave	Calculated for RbBr.Br$_2$.
Rubidium	25.86	26.26
Bromine	73.09	73.73

RbCl.Br$_2$.

This body is prepared by adding bromine to a warm, saturated solution of rubidium chloride until some bromine remains undissolved, and cooling to a low temperature. The compound crystallizes well, but it is the most unstable of the seven rubidium trihalides that have been prepared, and, although it was not fully dried, the sample used for analysis suffered a considerable amount of decomposition.

	Analysis gave		Calculated for $RbCl.Br_2$.
Rubidium	32.57	. . .	30.42
Chlorine	14.46	14.44	12.63
Bromine	49.04	49.40	56.93

In one attempt to prepare this trihalide too much water was used, and it was necessary to evaporate off the bromine and concentrate the solution. This operation was repeated several times, after fresh additions of bromine, before the proper conditions were arrived at, and the product finally obtained was contaminated with $RbBr.Br_2$, as is shown by the following analyses:

	Found.		Calculated for $RbCl.Br_2$.	Calculated for $RbBr.Br_2$.
Rubidium . . .	28.78	. . .	30.42	26.26
Chlorine . . .	7.66	6.94	12.63	0.
Bromine . . .	60.92	61.37	56.93	73.73

We have found by experiment that rubidium chloride is partly changed to bromide by evaporating an aqueous solution of it with bromine.* This explains the formation of the $RbBr.Br_2$.

Rb Cl. ClBr.

This compound can be prepared by adding 33 g. of bromine to a saturated solution of 50 g. of rubidium chloride, passing chlorine to saturation into the slightly warmed solution, and cooling to a low temperature. The substance is usually deposited in the form of very large, light yellow prisms.

	Analysis gave		Calculated for RbCl.ClBr.
Rubidium	35.42	35.41	36.15
Chlorine	29.27	28.96	30.02
Bromine	31.56	31.39	33.82

KI.I_2.

This body can be made in a few hours by dissolving the theoretical amount of iodine in a hot, saturated, aqueous solu-

* This is in accordance with the results of Potilzin referred to by Mendeléeff in his "Grundlagen der Chemie" (German ed., 1891), p. 538.

tion of potassium iodide and exposing the resulting solution to a winter temperature. It can also be made, as Johnson states,* by evaporating the solution in a desiccator for a long time. Johnson states that he always obtained a crop of potassium iodide before the triiodide separated. We have never obtained such a product, undoubtedly because we have invariably used a sufficient amount of iodine.

It was not considered necessary to make a new analysis of this body.

KBr.BrI.

This compound can be prepared by making a very concentrated, warm solution of the calculated amounts of potassium bromide, bromine, and iodine, and exposing it for some time to a low temperature. The product used for analysis was well crystallized, but it suffered rapid decomposition on exposure to the air.

	Analysis gave		Calculated for KBr.BrI.
Potassium	12.21	. . .	11.99
Bromine	51.25	51.61	49.06
Iodine	30.42	29.11	38.94

KCl.ClI.

To prepare this substance, chlorine is passed into a warm mixture of calculated quantities of potassium chloride and iodine, in the presence of an amount of water insufficient to dissolve the potassium chloride even when hot. The stream of chlorine is stopped as soon as the iodine has been converted into the monochloride, for otherwise Filhol's well-known compound $KCl.Cl_3I$ will be formed. Everything is then dissolved by warming and cautiously adding water if necessary, and the solution is exposed to a low winter-temperature. The crystals are very unstable, but apparently not quite as much so as KBr.BrI.

	Analysis gave		Calculated for KCl.ClI.
Potassium	15.29	15.35	16.49
Chlorine	27.53	27.50	29.94
Iodine	50.37	50.12	53.56

* Loc. cit.

Other Double Halides.

The double salt CsI.AgI was described in connection with the cæsium trihalides as being isomorphous with them as far as the crystals could be measured. Much work has since been done, without avail, in the hope of obtaining better crystals of this compound. Unsuccessful efforts have been made to obtain measurable crystals of all the corresponding silver double halides (except the fluorides) with cæsium, rubidium, and potassium. Two or three of these compounds had already been described, and it is probable that we could have proven the existence of all the rest of them, but the poorly crystallized products obtained had no interest in this connection and were not analyzed. Repeated efforts also failed to produce from potassium iodide and cuprous iodide a double salt that could be measured.

Theoretical.

Arguments were given in the article on the cæsium series which have led us to regard the trihalides as belonging to the class of bodies called double halides. We have indicated this view in the present article by using the usual formulæ for such compounds.

The well-known idea of a linking group of two halogen atoms as an explanation of the structure of double halides was advocated for the cæsium trihalides, and, since the rubidium and potassium compounds are entirely analogous, it is unnecessary to give their structural formulæ here. We believe, however, that the trihalides throw some light upon the constitution of the diatomic linking group. Remsen says,* "I cannot see that at present we have any evidence which justifies us in the use of the expression $-Cl=Cl-$ rather than $-Cl-Cl-$." If, as we believe, the structure of rubidium triiodide is expressed by the formula $Rb-(II)-I$, the structure of the linking group probably cannot be $-I-I-$; for in that case a single bivalent iodine atom could do the linking as well as a group of two, and we should expect the existence of diiodides,

* Amer. Chem. Jour., xi, 312.

no evidence of which, or of any other dihalide, has been found in the course of an elaborate investigation of the alkali-metal polyhalides. Moreover, with the assumption of bivalent halogen atoms, there would be no difficulty in supposing four halogens to be linked together, and the existence of tetrahalides would be anticipated. Our investigations, however, have shown the existence of only tri- and pentahalides.* The double linking seems therefore the more probable of the two forms mentioned by Remsen, but it may be added that any union weaker or stronger than the others in the molecule, and *different from them*, would also explain the non-existence of dihalides and tetrahalides.

Assuming that there is a linking group of two halogen atoms in the trihalides, the view advanced from a consideration of the cæsium compounds, that the most stable bodies have identical atoms in this group, is confirmed by the study of the rubidium and potassium analogues. For, on this assumption, all the potassium compounds which could be made contain a group of identical atoms, while in the missing rubidium compound they are dissimilar.

SHEFFIELD SCIENTIFIC SCHOOL,
March, 1892.

* The pentahalides will be described in a future article.

ON THE ALKALI-METAL PENTAHALIDES.*

By H. L. WELLS and H. L. WHEELER.

WITH THEIR CRYSTALLOGRAPHY.

By S. L. PENFIELD.

In the course of our investigations on the alkaline trihalides,† the compounds $CsCl.Cl_3I$, $RbCl.Cl_3I$, and $KCl.Cl_3I$ were encountered. The potassium compound had been described many years ago by Filhol.‡ This investigator prepared also the body $NH_4Cl.Cl_3I$ and obtained a similar magnesium compound, probably $MgCl_2.2Cl_3I.5H_2O$. He failed in his attempts to make analogous compounds with sodium and a considerable number of the other common metals.

It was evident from the peculiar behavior of cæsium tribromide and triiodide, mention of which was made in one of our previous articles,§ that a still higher bromide and iodide existed. These have now been identified as pentahalides.

In addition to these bodies, we have prepared the sodium and lithium analogues of Filhol's salt. They differ from all the other polyhalides that we have studied, in containing water of crystallization.

A large number of other alkaline pentahalides are theoretically possible, but, although we have made numerous experiments with the view of making the most promising of these, we have been unable to prepare them. It may be stated that special efforts were made to obtain potassium and rubidium pentaiodides.

* Amer. Jour. Sci., xliv, July, 1892.
† Ibid., III, xliii, 17 and 475.
‡ J. Pharm., xxv (1839), 431.
§ Amer. Jour. Sci., III, xliii, 24 and 27.

CsI_5.

This is produced, in an impure state as a black liquid solidifying at about 73°, by treating cæsium triiodide with hot water, and also by treating solid iodine with a hot solution of cæsium iodide. Artificial mixtures of cæsium triiodide and iodine, representing compositions varying from CsI_4 to CsI_9, all melt at a uniform temperature of about 73°. It is evident from this that the composition of the black liquid cannot be determined from its melting-point.

Cæsium triiodide, which is readily soluble in alcohol, becomes much more soluble in that liquid in the presence of two atoms of iodine to the molecule. A very concentrated solution of this kind gives crystals of the pentaiodide by cooling, but a much better product is obtained by concentration over sulphuric acid, using a slight excess of iodine to allow for loss by volatilization. The crystals are well formed and have a brilliant black color. They can be distinguished from crystals of iodine, which may separate if too much of this substance has been used, by their brittleness as well as their form. The substance melts, not sharply, at 73°. It loses iodine on exposure about as rapidly as iodine itself volatilizes. It does not contain water or alcohol.

Samples of the crystals quickly dried with paper gave the following results on analysis:

	Made by cooling.	By evaporation. Separate products.		Calculated for CsI_5.
Cæsium . . .	15.20	20.96	16.02	17.32
Iodine	. . .	. . .	. . .	82.68

$CsBr_5$.

When a concentrated solution of cæsium bromide is shaken up with a large excess of bromine, there is no separation of cæsium tribromide, as is the case when the theoretical amount of bromine is used. A large part of the cæsium bromide goes into solution in the liquid bromine and, on taking up a sufficient quantity of cæsium bromide, this solution becomes lighter in color than pure bromine.

A solution of cæsium bromide in bromine, made in the manner above indicated, was allowed to evaporate spontaneously at a temperature below 0°. A dark red solid finally separated, and it was prepared for analysis by pressing with papers at the same low temperature. After the adhering bromine had been removed, the substance gave off bromine-vapor very rapidly.

	Analysis gave	Calculated for $CsBr_5$.
Cæsium	29.93	24.95
Bromine		75.05

The analysis corresponds with the formula $CsBr_5$ as well as could be expected, considering the great instability of the compound.

$CsCl.Cl_3I$.

This substance can be prepared by dissolving 40 g. of cæsium chloride in a mixture of 600 c.c. of water and 200 c.c. of concentrated hydrochloric acid, adding 30 g. of iodine (one atom), and passing chlorine to saturation; meanwhile keeping the solution warm enough to dissolve any of the compound which separates in the form of a yellow precipitate, and finally cooling to crystallization. The hydrochloric acid is used to prevent the simultaneous deposition of an acid cæsium iodate.

	Analysis gave	Calculated for $CsCl.Cl_3I$.
Cæsium	32.44	33.09
Chlorine	34.79	35.32
Iodine	31.11	31.59

The crystals are of a pale orange color. They are in the form of slender prisms, usually in parallel position forming plate-like groups. The body is sparingly soluble in water and can be recrystallized from it without much decomposition. It is nearly permanent in the air. On heating, it is apparently converted into CsCl.ClI, for it melts like that substance at 238° (uncorr.) in the open capillary tube.

RbCl.Cl$_3$I.

This body can be conveniently prepared by adding 40 g. of iodine to a nearly saturated solution of 38 g. of rubidium chloride and passing in an excess of chlorine. The solution becomes warm from the reaction and, on cooling, large orange-yellow plates are deposited.

	Analysis gave		Calculated for RbCl.Cl$_3$I.
Rubidium	24.12	23.63	24.11
Chlorine	39.00	. . .	40.05
Iodine	35.31	. . .	35.83

The compound is soluble in alcohol, but unaffected by ether. When rapidly heated in an open capillary tube, it melts at 213° (uncorr.), undergoing some decomposition, and becomes completely white at about 270°. These numbers agree quite closely with the melting and whitening points of RbCl.ClI, so that it is evident that there is a loss of two atoms of chlorine before much further decomposition takes place. In view of this fact, it is remarkable that, when samples of RbCl.Cl$_3$I and RbCl.ClI were exposed to the air side by side for three months, the compound containing the greater amount of chlorine was almost completely decomposed, while the other remained nearly unchanged. It is therefore probable that RbCl.Cl$_3$I decomposes at ordinary temperatures by losing Cl$_3$I as a whole, while by heating another decomposition takes place.

KCl.Cl$_3$I.

This compound, first described by Filhol, has been prepared for the sake of studying its crystalline form. It is easily made by the method which has been given for the corresponding rubidium compound. The crystals obtained by cooling are in the form of very slender needles, but, by evaporating the mother-liquor from these at ordinary temperature, thicker prisms suitable for measurement can be obtained.

	Analysis gave	Calculated for $KCl.Cl_3I$.
Potassium	11.98	12.66
Chlorine	45.31	46.10
Iodine	42.50	41.23

$NaCl.Cl_3I.2H_2O$.

To prepare this substance, sodium chloride and iodine, in the calculated proportions, are mixed with an amount of water insufficient to dissolve the sodium chloride even on heating, chlorine is added to saturation at a gentle heat, and the liquid is filtered while still warm. The solution, on cooling to a low winter temperature, gives a crop of slender needles, but better crystals are obtained by evaporation in a desiccator. Some of the latter, quickly dried on paper, gave the following results on analysis:

	Found.	Calculated for $NaCl.Cl_3I.2H_2O$.
Sodium	7.17	7.01
Chlorine	42.92	43.29
Iodine	38.23	38.71
Water	12.84*	10.97

The water was determined by direct weighing in a calcium chloride tube, the halogens being retained by an ignited mixture of lead oxide and lead chromate.

The body is rapidly decomposed by exposure. It melts gradually between 70° and 90° and becomes white at about 115°. It is decomposed by strong alcohol and by ether.

$LiCl.Cl_3I.4H_2O$.

This was made by adding 60 g. of iodine to a hot saturated solution of 20 g. of lithium chloride in dilute hydrochloric acid, saturating with chlorine and cooling. A large quantity of long yellow needles was thus obtained. On evaporating the mother-liquor in a desiccator, larger prisms were deposited.

* Determined in a separate sample.

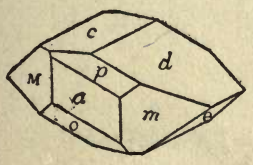
	Analysis gave		Calculated for $LiCl.Cl_3I.4H_2O$.
Lithium	2.03	2.16	2.01
Chlorine	39.96	39.94	40.80
Iodine	37.54	36.77	36.49
Water	20.93	. . .	20.68

On exposure to the air the substance quickly deliquesces, forming a yellow liquid. This gradually loses its color, finally leaving a solution of lithium chloride. The body melts at 70–80° and becomes white at about 180°. The crystals of this compound were not measured.

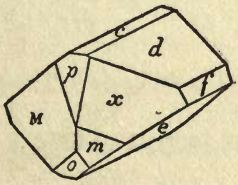
Crystallography.

The crystallization of CsI_5 is triclinic. By slow evaporation of solution in a desiccator, crystals were obtained which were about 10 mm. in diameter. Two crops were examined, in one of which the habit shown in Fig. 1 prevailed, while in the second the crystals were more highly modified, like Figs. 2 and 3.

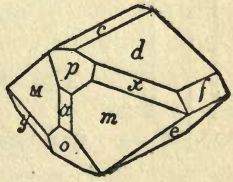
1.



2.



3.



The forms which were observed are:

a,	100,	i-$\breve{\imath}$	*d*, 011,	1-$\breve{\imath}'$	*o*, $\bar{3}11$, 3-$\bar{3}'$
c,	001,	*O*	*f*, 041,	4-$\breve{\imath}'$	*x*, 341, -4-$\frac{\breve{\imath}}{3}'$
m,	110,	*I'*	*e*, $0\bar{2}1$,	2-$\breve{\imath}$	*y*, $\bar{3}41$, 4-$\frac{\breve{\imath}}{3}'$
M,	$1\bar{1}0$,	*I*	*p*, 311,	-3-$\bar{3}'$	

The axial ratio is as follows:

$$\breve{a} : \bar{b} : \dot{c} = 0.9890 : 1 : 0.42765$$

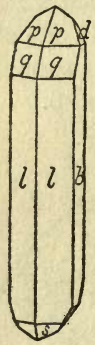
$$\alpha = 96° 56' \qquad \beta = 89° 55\tfrac{1}{2}' \qquad \gamma = 90° 21\tfrac{1}{2}'$$

The crystals gave good reflections of the signal on the goniometer. In the following tables the measurements which were chosen as fundamental are indicated by an asterisk:

		Measured.	Calculated.
$a \wedge c$,	$100 \wedge 001 =$	*90° 2′	
$m \wedge M$,	$110 \wedge 1\bar{1}0 =$	*89° 47′	
$a \wedge m$,	$100 \wedge 110 =$	*44° 43′	
$c \wedge e$,	$001 \wedge 02\bar{1} =$	*43° 26′	
$e \wedge d$,	$0\bar{2}1 \wedge 011 =$	*65° 25′	
$a \wedge M$,	$100 \wedge 1\bar{1}0 =$	45° 4′	45° 4′
$a \wedge e$,	$100 \wedge 02\bar{1} =$	90° 6′	90° 16′
$a \wedge d$,	$100 \wedge 011 =$	89° 57′	89° 54′
$a \wedge p$,	$100 \wedge 311 =$	41° 18′	41° 19′
$a \wedge o$,	$\bar{1}00 \wedge \bar{3}11 =$	41° 31′	41° 25′

		Measured.	Calculated.
$c \wedge m$,	$001 \wedge 110 =$	85° 8′	85° 9′
$c \wedge M$,	$001 \wedge 1\bar{1}0 =$	85° 7′	85° 7½′
$e \wedge m$,	$0\bar{2}1 \wedge \bar{1}\bar{1}0 =$	65° 9′	65° 3′
$e \wedge M$,	$02\bar{1} \wedge 1\bar{1}0 =$	65° 8′	65° 18′
$d \wedge m$,	$011 \wedge 110 =$	70° 3′	70° 2′
$d \wedge M$,	$011 \wedge \bar{1}10 =$	70° 6′	70° 4′
$p \wedge m$,	$311 \wedge 110 =$	40° 41′	40° 41′
$f \wedge d$,	$041 \wedge 011 =$	32° 30′	32° 37½′
$x \wedge m$,	$341 \wedge 110 =$	25° 46′	25° 44½′
$y \wedge M$,	$\bar{3}41 \wedge \bar{1}10 =$	25° 56′	25° 52′

4.



The form of $CsCl.Cl_3I$ is monoclinic. From a number of crystallizations this salt was always obtained in needles, sometimes over 20 mm. in length and having the habit shown in Fig. 4.

The forms which were observed are:

b,	010,	*i*-$\bar{\imath}$	*p*, 212,	−1-$\bar{2}$	*s*, $\bar{2}11$, 2-$\bar{2}$
l,	210,	*i*-$\bar{2}$	*q*, 211,	−2-$\bar{2}$	*d*, 041, 4-$\check{r}$

The axial ratio is as follows:

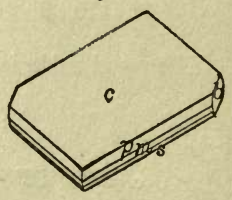
$$\dot{a} : \bar{b} : \dot{c} = 0.9423 : 1 : 0.4277, \beta = 100 \wedge 001 = 86° 20'$$

		Measured.	Calculated.
$l \wedge l$,	$210 \wedge 2\bar{1}0 =$	*50° 22′	
$l \wedge p$,	$210 \wedge 212 =$	*44° 51′	
$p \wedge s$,	$212 \wedge \bar{2}\bar{1}1 =$	*106° 35′	
$l \wedge q$,	$210 \wedge 211 =$	27° 3′	27° 7′

		Measured.	Calculated.
$l \wedge s$,	$\bar{2}\bar{1}0 \wedge \bar{2}\bar{1}1 =$	28° 35′	28° 34′
$p \wedge p$,	$212 \wedge 2\bar{1}2 =$	32° 59′	33° 2′
$p \wedge b$,	$212 \wedge 010 =$	73° 31′	73° 29′
$b \wedge d$,	$010 \wedge 041 =$	31° 0′	30° 21′

The crystallization of $RbCl.Cl_3I$ is monoclinic. This salt was crystallized a great many times, and was always obtained in plates, sometimes over 20 mm. broad, but seldom 1 mm. thick. The habit is shown in Fig. 5.

5.



The forms which were observed are:

$\bar{b}$, 010, i-$\bar{\imath}$	m, 110, I	s, $\bar{1}11$, 1
c, 001, O	p, 111, -1	

The axial ratio is as follows:

$$\dot{a} : \bar{b} : \dot{c} = 1.1390 : 1 : 1.975, \quad \beta = 100 \wedge 001 = 67° 6\tfrac{1}{2}'$$

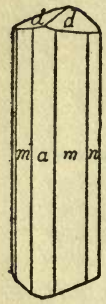
	Measured.		Measured.	Calculated.
$c \wedge m$, 001 $\wedge$ 110	= *74° 26′	$c \wedge s$, 001 $\wedge$ $\bar{1}11$	= 82° 12′	82° 15′
$c \wedge p$, 001 $\wedge$ 111	= *55° 20′	$s \wedge m$, $\bar{1}11$ $\wedge$ $\bar{1}10$	= 23° 20′	23° 19′
$p \wedge p$, 111 $\wedge$ $1\bar{1}1$	= *76° 21′	$p \wedge m$, 111 $\wedge$ 110	= 19° 5′	19° 6′

With the polarizing microscope the plates show an extinction parallel to their diagonals. In convergent light nothing of the ring system can be seen, but a dark bar crosses the field in the direction of the symmetry plane, indicating that the plane of the optical axes is the clino-pinacoid.

The crystalline habits and axial ratios of $CsCl.Cl_3I$ and $RbCl.Cl_3I$ are wholly different, and all attempts to find any similarity or mathematical relation between them has failed. We have endeavored to detect any hidden relation that might exist by examining separate crops of crystals, made from a solution containing both salts. Each form alone and mixtures of both were thus obtained, but no crystals of an intermediate form could be produced. One unmixed crop, having the form and angles of $CsCl.Cl_3I$, contained about sixteen per cent of $RbCl.Cl_3I$, while another, having the form and angles of $RbCl.Cl_3I$, contained about eleven per cent of $CsCl.Cl_3I$. These results show that isomorphous mixtures can be obtained of either form, depending upon which salt predominates, while the absence of any intermediate forms, and the inability to detect any mathematical relation between the two kinds of crystals, lead us to believe that the compounds are dimorphous.

The form of $KCl.Cl_3I$ is monoclinic. This salt was repeatedly made in fine needle-like crystals, too small to measure, by allowing a warm saturated solution to crystallize. By slow evaporation in a desiccator, at ordinary temperatures, stouter prismatic crystals, over 20 mm. long and 2 mm. in

6.



diameter were obtained, having the habit shown in Fig. 6. These gave excellent reflections and were measured without difficulty at winter temperature.

The forms which were observed are:

a, 100, $i\text{-}\bar{i}$	n, 120, $i\text{-}\breve{2}$
m, 110, I	d, 023, $\frac{2}{3}\text{-}\breve{i}$

The axial ratio is as follows:

$$\dot{a} : \bar{b} : \dot{c} = 0.9268 : 1 : 0.44725, \beta = 100 \wedge 001 = 84° 18'$$

	Measured.		Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$	$= *85° 22'$	$a \wedge d$, $100 \wedge 023$	$= *84° 32'$	
$d \wedge d$, $023 \wedge 0\bar{2}3$	$= *33° 3'$	$n \wedge n$, $120 \wedge \bar{1}20$	$= 56° 58'$	$56° 56'$

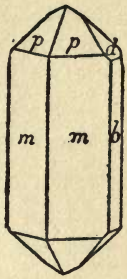
The positions and crystal symbols which have been adopted for this and the corresponding cæsium salt were chosen to show a similarity in the axial ratios. Both salts are alike in having a prismatic habit, but the forms which occur on each are quite different. If it were not for bringing out this similarity in axial ratios, the crystallography of both salts could be simplified somewhat by giving to the dome d above the simpler indices 011, and by taking the prism and pyramids of the cæsium salt as belonging to the unit instead of to the macrodiagonal series.

The anhydrous alkali-metal pentahalides do not form a well-defined crystallographic series, yet there are relations between three of them which seem to us to be more than coincidences. The similarity is shown in the following table:

$CsCl.Cl_3I$	Monoclinic	$\dot{a} : \bar{b} : \dot{c} = 0.9423 : 1 : 0.4277$, $\beta = 86° 20'$
$KCl.Cl_3I$	"	$\dot{a} : \bar{b} : \dot{c} = 0.9268 : 1 : 0.44725$, $\beta = 84° 18'$
CsI_5	Triclinic	$\breve{a} : \bar{b} : \dot{c} = 0.9890 : 1 : 0.42765$; $\alpha = 96° 56'$, $\beta = 89° 55\frac{1}{2}'$, $\gamma = 90° 21\frac{1}{2}'$

The crystallization of $NaCl.Cl_3I.2H_2O$ is orthorhombic. By slow evaporation of a solution in a desiccator, crystals were formed over 10 mm. in length, having the habit shown in Fig. 7.

7.



The forms which were observed are:

b, 010, *i-ĭ*	*p*, 111, 1
m, 110, *I*	*d*, 021, 2-$\breve{r}$

The axial ratio is as follows:

$$\breve{a} : \dot{b} : \dot{c} = 0.6745 : 1 : 0.5263$$

The crystals were measured at a temperature near 0° C. and gave excellent reflections.

Measured.		Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$	= *68° 0′	$m \wedge b$, $110 \wedge 010$ = 56° 0′	56° 0′
$m \wedge p$, $110 \wedge 111$	= *46° 44′	$b \wedge d$, $010 \wedge 021$ = 43° 29′	43° 32′

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1892.

ON SOME ALKALINE IODATES.*

By H. L. WHEELER.

WITH CRYSTALLOGRAPHIC NOTES.

By S. L. PENFIELD.

WHILE work on the compounds of iodine trichloride with alkaline chlorides † was in progress in this laboratory, it was noticed in making $KIC.Cl_3I$, $RbCl.Cl_3I$, and $CsCl.Cl_3I$ that white crystals were often formed under certain conditions. These compounds proved to be $KCl.KIO_3.HIO_3$, $RbCl.HIO_3$, and $2CsIO_3.I_2O_5$. Since they were not analogous, although formed under similar conditions, and since the rubidium and cæsium salts have not been described, an investigation of them was undertaken. Attempts to prepare these compounds by other methods led to the discovery of several other iodates. The new compounds that have been prepared are as follows:

$RbIO_3$	$CsIO_3$
$RbIO_3.HIO_3$	$2CsIO_3.I_2O_5$
$RbIO_3.2HIO_3$	$2CsIO_3.I_2O_5.2HIO_3$
$RbCl.HIO_3$	$CsCl.HIO_3$
$3RbCl.2HIO_3$	

The compound which separated from the solution of the potassium pentahalide has already been described, but since this is a new method of preparation, and since there are conflicting statements concerning its state of hydration, it has been re-investigated.

The results of the investigation of the rubidium salts show that the normal iodate is the only one of the series that can be recrystallized unaltered from an aqueous solution. In the

* Amer. Jour. Sci., xliv, August, 1892. † Ibid., p. 42.

case of the cæsium compounds, the normal iodate and the salt $2CsIO_3.I_2O_5$ are not decomposed by water. The other cæsium iodates give $2CsIO_3.I_2O_5$ when recrystallized from water, and not the normal iodate, thus showing an interesting difference between the rubidium and cæsium compounds.

It is the tendency of the acid rubidium iodates to separate in a higher state of hydration than the corresponding cæsium compounds.

It is also an interesting fact that the formation of the compounds of normal chloride and iodic acid was not observed on mixing the constituents. In the case of rubidium, products were obtained which proved to be $RbIO_3$, $RbIO_3.HIO_3$, or $RbIO_3.2HIO_3$, according to the concentration of the solutions and the excess of RbCl or HIO_3. On the other hand, by adding hydrochloric acid to a solution of rubidium iodate, if the acid is dilute $RbIO_3.2HIO_3$ is formed, while if concentrated the iodate is completely decomposed. Similar experiments, undertaken with cæsium chloride and iodic acid, did not give the peculiar double compound $CsCl.HIO_3$, but resulted in each case in the formation of $2CsIO_3.I_2O_5$.

Method of Analysis. — After the substances were prepared for analysis as described in detail beyond, the halogens were determined by first reducing the solution of iodate with sulphur dioxide, then precipitating with silver nitrate in the presence of nitric acid. This precipitate was then heated in a stream of chlorine, thus combining the test for chlorine and its determination in one operation. In the filtrate from the silver precipitate, the alkali metal was determined as sulphate after the removal of the excess of silver by means of hydrogen sulphide. Oxygen was determined in a separate portion by precipitation with silver sulphate, drying the precipitate at 100°, and then determining the loss on ignition. Duplicate halogen determinations were then made in this residue. In the case of the compounds containing the group I_2O_3, where an error would be introduced if the oxygen was determined in this manner, the substance itself was ignited and the oxygen calculated from the loss. The presence of water in these com-

pounds was determined by directly weighing it in a calcium-chloride tube, the substance being ignited in a combustion tube containing a mixture of lead chromate and lead oxide.

Normal Rubidium Iodate, $RbIO_3$. — This compound was made by adding one molecule of iodine pentoxide in either strong or dilute aqueous solution, to a solution of one molecule of rubidium carbonate. If the solutions are strong the iodate separates as a sandy precipitate, but if they are hot and dilute it separates on cooling in small grains or as a crystalline crust. At 23°, 100 parts of water dissolve 2.1 parts of the salt. The compound, after filtering on the pump, washing with a little water and drying on paper, gave the following results on analysis:

	Found.	Calculated for $RbIO_3$.
Rubidium	32.17	32.82
Iodine	48.50	48.75
Oxygen	20.59	18.43

The salt decrepitates strongly when heated, then melts, gives off oxygen but no iodine, and the residue is rubidium iodide. Hydrochloric acid readily dissolves it in the cold to a faint yellow-colored solution which increases in color on standing. On warming, chlorine is evolved and the solution turns bright yellow from the formation of iodine trichloride. If boiled with strong hydrochloric acid, RbCl.ClI * is formed, which separates on cooling.

The formation of normal rubidium iodate was also observed when a hot dilute aqueous solution of iodine trichloride was treated with rubidium carbonate. The compound thus obtained gave 48.43 per cent of iodine on analysis. It was formed also by dissolving the acid iodate in a strong, hot solution of rubidium chloride, and allowing the mixture to crystallize. This was identified by a rubidium determination which gave 32.58 per cent. In general, the iodates of rubidium all give this body when they are dissolved in hot water and the solutions left to crystallize. The products obtained

* Amer. Jour. Sci., xliii, 475.

in this manner decrepitated on heating and did not give off iodine. A rubidium determination in the substance obtained from $RbCl.HIO_3$ gave 32.76 per cent; from $3RbCl.2HIO_3$, 32.22 per cent.

Acid Rubidium Iodate, $RbIO_3.HIO_3$. — This was obtained by mixing warm solutions of one molecule of iodine pentoxide and two molecules of rubidium chloride. The compound generally separates on cooling as a heavy crystalline powder. It is difficultly soluble in cold water. Hot water dissolves it more readily, and on cooling the normal iodate separates. It is insoluble in alcohol. The crystals were filtered on a pump and washed with a little cold water and then pressed on paper. An analysis of these dried at 100° gave the following results, the oxygen being determined by difference.

	Found.	Calculated for $RbIO_3.HIO_3$.
Rubidium	20.13	19.58
Iodine	58.12	58.19
Oxygen	21.46	21.99
Hydrogen	0.29	0.23

The reaction which takes place in the preparation of this compound is probably according to the following equation:

$$RbCl + 2HIO_3 = RbIO_3.HIO_3 + HCl$$

The hydrochloric acid thus liberated reacts on a part of the iodic acid, chlorine is evolved, and the solution becomes yellow. When heated it does not decrepitate, but melts to a yellow mass, gives off water, then iodine, and finally froths with the evolution of oxygen. The residue consists of rubidium iodide.

Diacid Rubidium Iodate, $RbIO_3.2HIO_3$. — For the preparation of this compound, 5 g. of $RbIO_3$ were dissolved in 50 c. c. of water with the aid of heat, then 13 g. of iodine pentoxide in 50 c. c. of water were added, the mixture boiled down to half its volume and allowed to cool. The body separates as a heavy, crystalline powder. It is difficultly soluble in cold water. When dissolved in hot water and

the solution left to crystallize, $RbIO_3$ separates. The product obtained, as stated above, was separated from the mother-liquor by filtering on the pump, washed with a little cold water and dried at 100°.

	Found.		Calculated for $RbIO_3.2HIO_3$.
Rubidium	13.93	14.13	13.96
Iodine	61.91	62.48	62.20
Oxygen	23.74	. . .	23.51
Hydrogen	0.42	. . .	0.33

This compound does not lose water at 100°. When heated it does not decrepitate, but melts, gives off water, then iodine and oxygen, leaving a residue of rubidium iodide. The compound was also obtained by adding 10 c. c. of hydrochloric acid sp. gr. 1.1 to 5 g. of $RbIO_3$ in 20 c. c. of water. The mixture was warmed until all the $RbIO_3$ dissolved, when it gave a faint yellow solution which slowly deepened in color. On standing, a well-crystallized product of the compound under consideration was obtained, containing 14.13 per cent of rubidium and 62.19 per cent of iodine.

The addition of a saturated solution of rubidium chloride to syrupy iodic acid produces a precipitate which dissolves again in the excess of iodic acid. When more rubidium chloride is added, the whole being kept over a lamp, a point is reached where a precipitate begins to form in the hot solution. This is the compound in question. It was identified by a rubidium and an iodine determination. This gave 14.17 per cent of rubidium and 61.83 per cent of iodine.

$RbCl.HIO_3$. — This salt can be made by simply allowing a saturated solution of $RbCl.Cl_3I$ to stand for some hours, when large colorless prisms form, attached to the plates of $RbCl.Cl_3I$. The solution, after removing the crystals, warming to dissolve the pentahalide and passing chlorine in again, does not yield a further deposit of the substance. This is explained by the fact that so much hydrochloric acid is formed in the solution that the formation of this compound is prevented. The crystals remain unaltered on exposure to the

air, but on treatment with cold water they are decomposed, losing their lustre and becoming white. The solution has an acid reaction towards litmus. The hot saturated solution of this compound gives the normal iodate on cooling. The material for analysis was mechanically separated from adhering $RbCl.Cl_3I$ and dried in the air.

	Found.		Calculated for $RbCl.HIO_3$.
Rubidium . . .	28.88	. . .	28.78
Iodine	42.29	42.62	42.76
Chlorine	12.09	12.13	11.95
Oxygen	16.33	. . .	16.16
Hydrogen . . .	. . .	0.26	0.33

This salt can also be prepared by adding a strong aqueous solution of rubidium hydrate to a strong solution of iodine trichloride in water. This gives at first a precipitate of the compound $3RbCl.2HIO_3$, and the solution left at rest for a few days gives the large well-developed crystals of $RbCl.HIO_3$ unmixed with $RbCl.Cl_3I$. These were identified by their crystalline form.

On warming the crystals with hydrochloric acid, $RbCl.Cl_3I$ is formed, probably according to the following equation:

$$RbCl.HIO_3 + 5HCl = RbCl.Cl_3I + 3H_2O + Cl_2$$

and the $RbCl.Cl_3I$, on further heating, gives RbCl.ClI with the liberation of chlorine. When the substance is heated it melts, gives off water, chloride of iodine, and oxygen; the residue consists of rubidium chloride and iodide. A determination of the halogens in this residue gave 3.52 per cent of chlorine and 53.66 per cent of iodine.

$3RbCl.2HIO_3$.—This compound, which is analogous to the sodium compound $3NaCl.2NaIO_3.9H_2O$, described by Rammelsberg,* and also to the salt $3NaI.2NaIO_3.19H_2O$, obtained by Penny,† or $3NaI.2NaIO_3.20H_2O$ according to Marignac,‡ except that it contains no water of crystallization, was pre-

* Pogg. Ann., xli, 548; cxv, 584. † Ann. Ch. Pharm., xxxvii, 202.
‡ Jabresb., 1857, 124: Ann. Min., V, ix, 1.

pared by two methods. It was obtained by the addition of a hot, strong, aqueous solution of rubidium hydroxide to a strong solution of iodine trichloride, the latter being in excess. The mixture was then filtered hot, and on cooling, a mass of fine needles separated. The mother-liquor, on standing, yielded the large crystals of $RbCl.HIO_3$. The needles are stable in the air and at 100°. From the hot, saturated, aqueous solution of the compound, the normal iodate separates on cooling.

The formation of this compound was also observed on adding a strong solution of rubidium carbonate to a hot, saturated solution of $RbCl.Cl_3I$, the latter being in excess. The colorless, slender, transparent needles, thus obtained, generally separate in groups radiating from a point on the surface of the yellow crystals of $RbCl.Cl_3I$. After separating the colorless crystals mechanically from the pentahalide, they were air-dried on paper and then analyzed, while the material obtained according to the previous method was dried at 100°.

	From RbOH and ICl_3.		From Rb_2CO_3 and $RbCl.Cl_3I$		Calculated for $3RbCl.2HIO_3$.
Rubidium,	35.41	34.58	35.78	. . .	35.87
Iodine,	35.27	36.00	35.87	35.81	35.52
Chlorine,	14.99	14.82	15.26	15.16	14.90
Oxygen,	. . .	13.15	. . .	13.64	13.43
Hydrogen,	. . .	0.29	. . .	0.30	0.28

When heated, the substance does not decrepitate, but melts, gives off chloride of iodine, and the residue consists of a mixture of rubidium chloride and iodide. A sample of this residue gave on analysis 9.68 per cent of chlorine and 38.91 per cent of iodine.

Normal Cæsium Iodate, $CsIO_3$. — This was prepared by adding a moderately strong aqueous solution of iodic acid to a strong solution of cæsium carbonate, care being taken to have the carbonate in excess. When all the iodic acid had been added, the solution was boiled. On cooling, a crystalline mass separated, consisting apparently of small cubes. At 24°, 100 parts water dissolve 2.6 parts of the salt. It is insoluble

in alcohol. The body was prepared for analysis by filtering on the pump, washing with cold water, and then pressing on paper and drying at 100°.

	Analysis gave		Calculated for $CsIO_3$.
Cæsium	43.08	43.53	43.18
Iodine	40.84	. . .	41.23
Oxygen	15.74	. . .	15.59

This was also obtained, in attempts to prepare a cæsium salt corresponding to $3RbCl.2HIO_3$, by adding cæsium hydrate or carbonate, in moderately strong aqueous solution, to a strong solution of iodine trichloride in excess, when it at once separated in the form of a white sandy precipitate, which under the microscope was seen to consist of transparent grains of indefinite form. Unless the iodine trichloride is nearly saturated with the carbonate, $CsCl.Cl_3I$ or $CsCl.ClI$ * is obtained, mixed with the iodate. An iodine and oxygen determination in the air-dried salt gave 40.55 and 40.83 per cent of iodine and 15.67 per cent of oxygen. When this iodate is heated, it does not give off iodine, but melts and evolves oxygen. The residue is cæsium iodide.

$2CsIO_3.I_2O_5$. — This substance can be prepared in pure condition and in large quantity by mixing a moderately dilute, aqueous solution of two molecules of cæsium chloride with one molecule of iodine pentoxide dissolved in a little water. Any precipitate that may have been produced is dissolved by the aid of heat and more water if necessary. On cooling, the compound separates as a sandy powder. This can be washed with water or recrystallized from hot water without decomposition. It can also be recrystallized from dilute solutions of iodic acid. At 21°, 100 parts of water dissolve 2.5 parts of this salt. It is insoluble in alcohol. The material for analysis was air-dried after pressing on paper.

	Found.	Calculated for $2CsIO_3.I_2O_5$.
Cæsium	27.93	28.00
Iodine	53.42	53.47
Oxygen	18.69	18.53

* Amer. Jour. Sci., III, xliii, 17, and xliv, 42.

This compound invariably separates along with the crystals of $CsCl.Cl_3I$, when the latter is prepared in the absence of hydrochloric acid, but the yield is not very large. It is thus obtained in the form of small, rounded, white nodules, which, on close inspection, are seen to occur in pairs, the two nodules being on opposite sides of a thin layer of the pentahalide. They were mechanically separated from the latter, no water being used to wash the compound when prepared for analysis. The following results are sufficient for its identification:

Cæsium	29.11
Iodine	50.21
Oxygen	18.99
Chlorine	3.24

This compound was also obtained by the following methods. By mixing 6 g. of $CsIO_3$, 20 c. c. of water, and 10 c. c. of HCl, sp. gr. 1.1. When the mixture was boiled, it became yellow and chlorine was evolved, and when cooled the substance separated as a crystalline crust. It was identified by a determination of cæsium which gave 28.40 per cent.

The compounds $2CsIO_3.I_2O_5.2HIO_3$ and $CsCl.HIO_3$ give this body when their hot saturated solutions are cooled. A cæsium determination in the products thus obtained gave 27.94 and 28.12 per cent respectively.

When this body is treated with hydrochloric acid, sp. gr. 1.1, the solution becomes yellow, evolves chlorine on warming, and, when concentrated on the water bath, yields on cooling well-crystallized CsCl.ClI. Analysis gave 50.63 per cent of cæsium chloride. (Calculated for CsCl.ClI, 50.90 per cent.)

When heated in a closed tube it gives no sign of water, gives off iodine, then melts with the evolution of iodine and oxygen. The residue consists of cæsium iodide.

$2CsIO_3.I_2O_5.2HIO_3$. —This body was obtained by adding 5 g. of $2CsIO_3.I_2O_5$ to a boiling solution of 25 g. of iodine pentoxide in sufficient water to form a syrup. Water was then added, and the precipitate thus produced proved to be the compound in question. Thus produced, it separates as

a finely divided amorphous precipitate, which can be dried in the air or at 100° without losing water. It is difficultly soluble in water and when crystallized from an aqueous solution gives $2CsIO_3.I_2O_5$. An analysis of the substance dried at 100° gave:

	Found.	Calculated for $2CsIO_3.I_2O_5.2HIO_3$.
Cæsium	19.71	20.43
Iodine	57.68	58.52
Oxygen	20.41	20.89
Hydrogen	0.12	0.16

Water determinations, in samples dried in the air on paper, gave 1.45 and 1.38 per cent; theory requires 1.44.

When the substance is heated it gives off water and iodine, then oxygen, the residue consisting of cæsium iodide.

$CsCl.HIO_3$. — This was obtained, in an attempt to increase the yield of $2CsIO_3.I_2O_5$, by adding a rather small quantity of cæsium carbonate to a hot, saturated solution of $CsCl.Cl_3I$, when, on cooling and allowing the mixture to stand, colorless, flat, transparent prisms separated on the yellow crystals of $CsCl.Cl_3I$ previously formed. These colorless prisms were picked out from the solution, dried on paper and separated mechanically, as far as possible, from any adhering $CsCl.Cl_3I$. These on analysis gave the following results:

	Found.		Calculated for $CsCl.HIO_3$.
Cæsium	38.09	. . .	38.60
Iodine	36.08	36.29	36.86
Chlorine	11.69	11.82	10.31
Oxygen	13.85	. . .	13.94
Hydrogen	0.30	. . .	0.29

The crystals remain unaltered on exposure to dry air, but on treating them with water they immediately become opaque. On recrystallizing from water they give $2CsIO_3.I_2O_5$. When the substance is heated, it gives off water and iodine chloride, melts, and gives off oxygen, the residue consisting of chloride and iodide of cæsium. When it is warmed with hydrochloric

acid, it undergoes the same decomposition as the corresponding rubidium compound.

$KCl.KIO_3.HIO_3$. — This compound has previously been prepared by treating KIO_3 with hydrochloric acid, or a solution of iodine trichloride with potassium hydrate or carbonate. It has been described by Serullas * and Rammelsberg † as anhydrous, and the formula $2KCl.2KIO_3.I_2O_5$ was assigned to the salt. Millon,‡ from his determination of potash in this salt, concluded that the substance contained a molecule of water, but he made no determination of it. Finally Marignac,§ who examined it more carefully, made a determination of the water by drying the substance at 100°, then igniting it in a tube with metallic copper and collecting and weighing the water by means of a sulphuric acid tube.

The compound obtained from a solution of $KCl.Cl_3I$ separated in shining transparent prisms, stable in the air. It contained water corresponding to the formula $2KCl.2KIO_3.I_2O_5.H_2O$ or $KCl.KIO_3.HIO_3$. An analysis of the air-dried salt gave the following results:

	Found.		Calculated for $KCl.KIO_3.HIO_3$.
Potassium	16.94	16.83	16.82
Iodine	54.46	. . .	54.66
Chlorine	7.72	. .	7.64
Oxygen	. . .	. . .	20.66
Hydrogen	0.20	. . .	0.22

This compound and the one obtained by Marignac are therefore identical.

On ignition it gives off water, iodine chloride, and oxygen, the residue consisting of potassium iodide and chloride. An analysis of this residue gave 2.39 per cent chlorine and 70.87 per cent iodine.

The author takes occasion here to express his obligations to Professor H. L. Wells for the use of the material in this in-

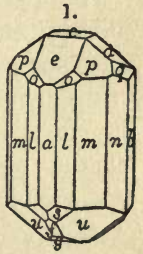
* Ann. Ch. Phys., II, xliii, 113. † Ibid., III, ix, 407.
‡ Pogg. Ann., xcvii.
§ Jahresb., 1856, 298. Ann. Min., V, ix, 1.

vestigation and for valuable suggestions; also to Professor S. L. Penfield, who has kindly furnished the crystallographical descriptions.

Notes on the Crystalline Form of $RbCl.HIO_3$ and $CsCl.HIO_3$.

Rb Cl.HIO₃

1.



The form of $RbCl.HIO_3$ is monoclinic. The crystals are highly modified, doubly terminated prisms, Fig. 1. The faces gave fair reflections, and the measurements which were chosen as fundamental are marked by an asterisk in the table of angles.

The axial ratio and forms are as follows:

$$\dot{a} : \bar{b} : \dot{c} = 0.9830 : 1 : 0.7577, \quad \beta = 100 \wedge 001 = 87° 56'$$
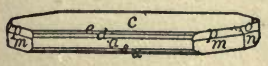
a, 100, $\dot{i}$-$\bar{i}$	*l*, 320, i-$\frac{3}{2}$	*d*, 011, 1-$\dot{a}$	*g*, $\bar{1}02$, $\frac{1}{2}$-$\bar{i}$	*q*, 142, $-2\dot{4}$
b, 010, $\dot{i}$-$\dot{a}$	*m*, 110, I	*e*, 101, -1-$\bar{i}$	*a*, 211, -2-$\bar{2}$	*s*, $\bar{2}11$, 2-$\bar{2}$
c, 001, 0	*n*, 120, $\dot{i}$-$\dot{2}$	*f*, $\bar{1}01$, 1-$\bar{i}$	*p*, 111, -1	*u*, $\bar{1}11$, 1.

	Measured.	Calculated.		Measured.	Calculated.
$a \wedge c$, $100 \wedge 001 =$	*87° 56′		$a \wedge d$, $100 \wedge 011 =$	88° 29′	88° 21′
$a \wedge e$, $100 \wedge 101 =$	*51° 5′		$a \wedge s$, $\bar{1}00 \wedge \bar{2}11 =$	38° 32′	39° 47′
$c \wedge d$, $001 \wedge 011 =$	*37° 8′		$a \wedge u$, $\bar{1}00 \wedge \bar{1}11 =$	59° 57′	59° 38′
$a \wedge l$, $100 \wedge 320 =$	33° 13′	33° 13′	$e \wedge p$, $101 \wedge 111 =$	30° 28′	30° 31′
$a \wedge m$, $100 \wedge 110 =$	44° 7′	44° 29½′	$f \wedge u$, $\bar{1}01 \wedge \bar{1}11 =$	31° 22½′	31° 24′
$a \wedge n$, $100 \wedge 120 =$	62° 42′	63° 1½′	$p \wedge q$, $111 \wedge 142 =$	26° 36′	26° 30′
$a \wedge o$, $100 \wedge 211 =$	38° 19′	38° 28½′	$c \wedge g$, $001 \wedge \bar{1}02 =$	21° 17′	21° 20′
$a \wedge p$, $100 \wedge 111 =$	57° 13′	57° 14′	$c \wedge f$, $001 \wedge \bar{1}01 =$	38° 26′	38° 23½′

Cs Cl.HIO₃

The form of $CsCl.HIO_3$ is monoclinic. The crystals, from the one crop which was examined, were about 5 mm. in length and had the habit shown in Fig. 2. They were attached at one end, and usually grew in radiating and divergent groups. The faces were not very perfect, and only approximate measurements could be made. Those which were chosen as fundamental are:

2.



$m \wedge m$, $110 \wedge \bar{1}10 = 90° 12'$ $m \wedge p$, $110 \wedge 221 = 24° 37'$ $a \wedge p$, $100 \wedge 221 = 49° 53$

The axial ratio and forms are as follows:

$$\dot{a} : \bar{b} : \dot{c} = 0.9965 : 1 : 0.7698 \qquad \beta = 100 \wedge 001 = 89° 53\tfrac{1}{2}'$$

a, 100, i-$\bar{i}$	m, 110, I	d, 403, $-\frac{4}{3}$-$\bar{i}$	s, $\bar{4}03$, $\frac{4}{3}$-$\bar{i}$	p, 221, -2
c, 001, 0	n, 130, $\grave{i}$-$\grave{3}$	e, 203, $-\frac{2}{3}$-$\bar{i}$	u, $\bar{2}03$, $\frac{2}{3}$-$\bar{i}$	o, 263, -2-$\grave{3}$

The pyramids p and o were frequently wanting. The orthodomes d, e, s, and u were very constant in their development and gave to the crystals an orthorhombic habit. Owing to the curved and striated character of the faces, the symmetry could not be satisfactorily determined by measurement, but the optical properties showed that the crystals were truly monoclinic. In polarized light the tables show an extinction parallel to the ortho-axis, and in convergent light one of the optical axes and the acute bisectrix can be seen near the limits of the field. The plane of the optical axes is the clino-pinacoid.

These two salts, although entirely different in crystalline habit, are very similar in their axial ratios.

Sheffield Scientific School,
April, 1892.

ON A METHOD FOR THE QUANTITATIVE DETERMINATION OF CÆSIUM, AND THE PREPARATION OF PURE CÆSIUM AND RUBIDIUM COMPOUNDS.*

By H. L. WELLS.

SINCE no method has heretofore been devised for the accurate quantitative determination of cæsium in the presence of both rubidium and potassium, some experiments have been made in order to test the availability of the plumbic chloride, described in a recent article,† for this purpose. The results have not been as accurate as could be desired, but the method will be useful until a better one is found.

The solubility of Cs_2PbCl_6 in a hydrochloric acid solution (fuming acid diluted with water 1 : 1), containing twice the theoretical amount of lead chloride and saturated with chlorine, was determined by making a precipitation of about 1 g. of Cs_2PbCl_6 under these conditions in 350 c. c. and determining the cæsium in the filtrate. The whole filtrate gave 0.0119 g. of Cs_2SO_4, which corresponds to a solubility of 0.000068 g. of Cs_2PbCl_6 in 1 c. c. A similar experiment in which concentrated hydrochloric acid was used, and also a larger excess of lead chloride, gave a solubility of 0.00049 g. of Cs_2PbCl_6 in 1 c. c. It has been shown in the article referred to that the solubility of Rb_2PbCl_6 is 0.003 g. in 1 c. c. under similar conditions.

Some actual determinations of cæsium were made as follows: Known quantities of Cs_2PbCl_6 and about an equal weight of $PbCl_2$ were dissolved in hot HCl (1 : 1). Chlorine was passed into the solutions until they became cold, and, after standing about three hours, the precipitates were collected in porcelain Gooch crucibles and washed with hydrochloric acid containing chlorine. The precipitates were decomposed with hot water,

* Amer. Jour. Sci., xlvi, September, 1893. † Ibid., p. 180.

and the cæsium in the resulting solutions was determined as sulphate. In one case a comparatively large amount of potassium chloride was present. The details are as follows:

	Cs_2PbCl_6 taken.	KCl taken.	Volume 1 : 1 HCl.	Cs_2SO_4 found.	Deficiency as Cs_2SO_4
	g.	g.	c. c.	g.	g
A	.1674	. .	35	.0856	.0026
B	.1592	. .	35	.0807	.0031
C	.1280	0.5	35	.0638	.0035

These results indicate greater errors than were expected from the previous solubility determinations. It is suspected that a little of the precipitate was dissolved by washing, and the use of hydrochloric acid containing lead chloride as well as chlorine would probably diminish the error. The last experiment shows that the presence of a considerable amount of potassium has no influence upon the result.

The determination of cæsium by this method can be simplified by weighing the precipitated cæsium-plumbic chloride directly. The salt is perfectly stable at 100°. The following table gives the details of a number of determinations made in this way. The precipitates were all thoroughly washed with hydrochloric acid containing chlorine and dried on an asbestos filter at 100°.

	Cs_2PbCl_6 taken.	$PbCl_2$ taken.	KCl taken.	Volume HCl.		Cs_2PbCl_6 found.	Cs_2PbCl_6 lost.
		g.	g.	c.c.		g.	g.
A	0.2761	0.25	. . .	28	1 : 1	0.2650	0.0111
B	0.0878	1.0	0.5	52	1 : 1	0.0833	0.0035
C	0.1202	1.0	. . .	52	1 : 1	0.1071	0.0131
D	0.7558	0.1	. . .	28	conc.	0.7369	0.0189
E	0.2483	0.1	. . .	20	conc.	0.2359	0.0124

The results show considerable losses in cæsium, which apparently do not entirely depend upon the volume in which the precipitation is made. It is believed that the losses occur chiefly in washing, for large quantities usually show a larger total loss than small ones.

When cæsium and rubidium are together, the precipitation of cæsium plumbic chloride is accompanied by a partial precipitation of the rubidium, unless the quantity of the latter is small. It is possible, however, to make an indirect determination of the cæsium in such a precipitate by weighing it and afterwards determining the weight of the cæsium and rubidium sulphates. Two experiments have been made on this plan, where not only rubidium, but also potassium, sodium, and lithium were present.

	A	B
	g.	g.
Cs_2PbCl_6 taken,	0.3561	0.1545
Rb_2PbCl_6 taken,	0.2845	0.4101

To each of these were added about 0.15 g. each of potassium and sodium chlorides, 0.25 g. of lithium carbonate, and 0.1 g. of lead chloride. The substances were dissolved by boiling with dilute hydrochloric acid, about an equal volume of concentrated acid was added, and chlorine was passed until the solutions became cold.

	A	B
	c. c.	c. c.
Volume of solution,	30	50

After standing several hours, the precipitates were collected on asbestos filters in porcelain Gooch crucibles, washed with dilute hydrochloric acid saturated with chlorine, dried at 100° and weighed.

	A	B
Cs_2PbCl_6 and Rb_2PbCl_6 found,	0.5621	0.4538

The precipitates were treated on the filters with hot water, the resulting solutions were evaporated with sulphuric acid, the lead sulphate was removed by filtration, the filtrates were evaporated and finally ignited in an ammoniacal atmosphere, and the mixed sulphates were weighed.

	A	B
Cs_2SO_4 and Rb_2SO_4 found,	0.2826	0.2164

For calculating the results, the following formulæ were used:

(P = weight of $Cs_2PbCl_6 + Rb_2PbCl_6$)
(S = weight of $Cs_2SO_4 + Rb_2SO_4$)
Weight of Cs = 5.095S — 2.301P
Weight of Rb = 2.006P — 3.801S

	A	B
Cæsium taken	0.1381	0.0599
Cæsium found	0.1464	0.0584
Error in cæsium	0.0083+	0.0015—
Rubidium taken	0.0823	0.1186
Rubidium precipitated . .	0.0534	0.0876

The results show that approximate determinations of cæsium can be made by this method when all the alkali-metals are present. The process leaves a part of the rubidium with the potassium, and these two metals can be precipitated as platinic chlorides and their amounts determined indirectly.

The method which has been described is useful for the extraction of cæsium and rubidium from their natural sources. The following method of procedure may be suggested, supposing all the alkali-metals to be present as chlorides in a concentrated aqueous solution:

At least an equal volume of concentrated hydrochloric acid is added, and any precipitated sodium and potassium chlorides are removed. The solution is diluted somewhat, to avoid a subsequent precipitation of these chlorides, a solution of lead chloride, made by boiling lead oxide with a large excess of hydrochloric acid, is gradually added, while chlorine is passed into the solution until it is cold and until fresh additions of lead chloride fail to produce a yellow precipitate. According to my solubility determinations, this precipitation leaves less than 1 g. of rubidium and a much smaller quantity of cæsium in each liter of the solution. The precipitate is usually almost free from potassium. To ensure the complete purification of the cæsium and rubidium, the precipitate is washed with hydrochloric acid containing chlorine and lead chloride, then it is treated repeatedly with small quantities of boiling water until completely decomposed, and the resulting solution is

subjected to a repetition of the foregoing process. The mixed plumbic salts are decomposed with hot water, and the resulting filtered solution is evaporated to dryness to remove hydrochloric acid. The residue is dissolved in hot water,* the lead is precipitated by the addition of a slight excess of ammonium sulphide, and the precipitate is removed by filtration. The solution is evaporated to dryness, and the residue consists of cæsium and rubidium chlorides and some ammonium chloride.

The following directions for the separation and purification of the cæsium and rubidium do not involve any new methods, but the course of procedure has been arrived at after a considerable amount of experience, and it may be of use to others. It is assumed that rubidium is more abundant than cæsium in the mixture. If cæsium predominated, it would be more advantageous to extract that metal first by an obvious modification of the process.

The mixed chlorides of rubidium and cæsium are dissolved in at least five parts of concentrated nitric acid, and the solution is evaporated to dryness and heated until the excess of nitric acid is removed. The residue is dissolved in a small amount of water, and as much oxalic acid as corresponds to twice the weight of the original chlorides is added. The whole is evaporated to dryness, and the residue is ignited in platinum until the oxalates are completely converted into carbonates.† The carbonates are dissolved in water, the solution is filtered and exactly neutralized with a measured solution of tartaric acid, as much more tartaric acid as has been used for the neutralization is added, and the solution is evaporated until it becomes saturated while hot. The solution on cooling deposits acid rubidium tartrate, which is washed with a small quantity of water and is recrystallized two or three times from a hot saturated solution, in the same way, until it gives no cæsium

* No part of this residue should be thrown away on the assumption that it is lead chloride, for the salt $CsPb_2Cl_5$ is difficultly soluble and resembles $PbCl_2$.

† This method of converting alkaline chlorides into carbonates is due to J. L. Smith, Amer. Jour. Sci., II, xvi, 373.

spectrum.* The united mother-liquors from the acid rubidium tartrate are evaporated to dryness and ignited in platinum. The resulting carbonates are converted into chlorides, and, to a solution of these in a small volume of 1 : 1 hydrochloric acid, a solution of antimony trichloride in the same acid is added as long as a precipitate forms.† The precipitate is collected on a filter and washed with hydrochloric acid. To remove traces of rubidium, the precipitate is thoroughly decomposed with successive, small quantities of hot water, then hydrochloric acid and a little antimony trichloride are added to the whole, in order to repeat the precipitation. The last precipitate is washed with hydrochloric acid. It usually shows no rubidium when tested with the spectroscope. The cæsium antimony chloride is decomposed with hot water, and hydrogen sulphide is passed into the resulting solution. The filtrate from the antimony sulphide gives, on evaporation, pure cæsium chloride. The filtrates from the antimony double salt are freed from antimony, evaporated to dryness, and the mixture of cæsium and rubidium chlorides, which should be very small in amount, is preserved for use in subsequent purifications.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1893.

* This method is due to O. D. Allen, Amer. Jour. Sci., II, xxxiv, 367.

† Method of Godeffroy, Berichte, vii, 375.

ON SOME PECULIAR HALIDES OF POTASSIUM AND LEAD.*

By H. L. WELLS.

In a recent article I have described a series of double chlorides of the type M_2PbCl_6, where M is NH_4, K, Rb and Cs. It has seemed desirable to extend the investigation by attempting to prepare bromides and iodides corresponding to these salts. A thorough search has been made, using the metals of the potassium group and sodium, with the result that no double bromides or iodides containing extra halogen could be prepared, except in the case of potassium. It is remarkable that the potassium-lead bromide and iodide which have been discovered do not correspond in composition to the chlorides. The failure to prepare double salts of rubidium and cæsium corresponding to the new potassium compounds was unexpected, for, as a general rule, the insolubility and stability and the consequent ease of preparation of such compounds become greater from potassium towards cæsium. The explanation of the anomaly probably lies in the fact that extremely concentrated rubidium and cæsium solutions containing a lead halide and the corresponding halogen cannot be obtained, in the case of the bromides and iodides, on account of the slight solubility of cæsium triiodide, and of the double halides which are formed with $PbBr_2$ and PbI_2.

The compounds to be described probably have the composition represented by the following formulæ:

$$K_3Pb_2I_8.4H_2O$$
$$K_3Pb_2Br_8.4H_2O$$

* Amer. Jour. Sci., xlvi, September, 1893.

These formulæ may be also written,

$$3KI.2PbI_2.I.4H_2O \text{ and } 3KBr.2PbBr_3.Br.4H_2O$$

The composition of these salts is very remarkable, on account of the small amount of the extra halogen that they contain. They apparently do not correspond to any other chemical compound that is known.

The Iodide, $K_3Pb_2I_8.4H_2O$. — This salt forms brilliant, black, prismatic crystals, sometimes a centimeter or two in length and three or four millimeters in diameter. Although the crystals have fine prismatic faces, they never appear to have definite terminations. The ends usually appear fibrous, as though made up of numerous small crystals in parallel position. When the crystals are crushed on paper it is evident that they enclose much mother-liquor. The salt is deposited from nearly, or quite, saturated solutions of potassium iodide containing lead iodide and iodine. It is deposited at ordinary temperature, usually slowly, after the lapse of several hours or even after several days. In preparing the compound, the lead iodide and the iodine can be varied considerably, but it is formed only in very concentrated potassium iodide solutions, and it is difficult to obtain crops of it which are not evidently contaminated with this salt in the form of crystals. The salt is stable in the air, but it is instantly decomposed by water or alcohol, so that it cannot be washed.

Six separate crops have been analyzed, and great care has been used in selecting them and in drying them on paper for analysis. In two cases the product was rapidly and finely pulverized during the drying operation, but without any effect upon its composition. The results of the six analyses agree with remarkable closeness, but in spite of this fact it must be assumed, from considerations which will be given subsequently, that all these products were seriously contaminated with potassium iodide. The fibrous nature of the crystals, and the concentration of the mother-liquor, make the possibility of such a contamination very evident, but the constancy of this contamination, as indicated by the uniformity of the analyses, is very

remarkable in view of the fact that some of the products were made at wide intervals of time, covering a period of about six months, so that there were considerable variations in the laboratory temperature.

The products were made under the following conditions:

	KI. g.	PbI_2. g.	I. g.	Volume. c. c.
A . . .	450	30	15	?
B . . .	425	30	50	450
C . . .	445	40	70	470
D . . .	445	40	100	470
E . . .	445	40	150	460
F . . .	200	15	15	200

They gave the following results on analysis:

	K.	Pb.	I.	H_2O.	
A . . .	9.31	22.03	64.00	4.69 =	100.03
B . . .	9.25	22.30	. . .	4.81	. . .
C . . .	9.07	22.03	63.98	4.89 =	99.97
D . . .	9.21	21.98	64.09	4.71 =	99.99
E . . .	9.20	22.13	64.17	. . .	. . .
F . . .	9.27	22.02	63.84	. . .	. . .

In these analyses, and those which follow, water was determined by weighing it directly in a calcium-chloride tube. The other determinations were made according to the methods mentioned in the preceding article on the double salts of lead tetrachloride.

The above analyses correspond closely to the formula $K_9Pb_4I_{19}.10H_2O$, but it will be shown beyond that the probable formula of the pure compound is $K_3Pb_2I_8.4H_4O$. This requires K = 7.25, Pb = 25.56, I = 62.74, and H_2O = 4.45. If this is the true composition, it must be assumed that all of the analyzed products were contaminated with about 16.5 per cent of potassium iodide, and that an excess of water was present, possibly on account of the hygroscopic properties of that salt.

It is to be noticed that the products were prepared under great variations in the amount of iodine present, and it can be safely assumed, from the care with which the products

were examined, that they were not contaminated with the salt $KPbI_3.2H_2O$ nor any similar compound. The amount of lead iodide in the solutions was comparatively small, and a large part of it was used in forming the salt under consideration, so that any contamination must have been chiefly potassium iodide. It is therefore evident, since the salt is not decomposed on exposure, and since the analyses show a constant amount of extra iodine in spite of the variations of this ingredient in the solutions, that the analyses must show the true ratio between the lead iodide and the extra iodine in the pure compound. This ratio is $2PbI_2 : I$ in both $K_9Pb_4I_{19}$ and $K_3Pb_2I_8$.

The Bromide, $K_3Pb_2Br_8.4H_2O$. — This compound forms dark brown, prismatic crystals, which are solid and definitely terminated, so that they do not have the tendency to hold inclosed mother-liquor which the iodide has. The salt is easily prepared and it crystallizes well, but it is extremely unstable. When exposed to the air, it begins to whiten almost instantly, giving off bromine. It is stable, however, in air containing a considerable amount of bromine vapor, so that it can be dried by pressing on paper in such an atmosphere. It is sufficiently stable, when corked up in a weighing-tube, to be rapidly weighed in a cold room without serious decomposition.

Three crops of the double bromide were analyzed. A and B were made, in each case, by adding 20 c. c. of bromine to 400 c. c. of a cold solution which was saturated with potassium bromide and lead bromide, and allowing the mixture to stand over night. C was made like the other crops, except that 30 c. c. of bromine were used.

	Found.			Calculated for $K_3Pb_2Br_8.4H_2O$.
	A.	B.	C.	
Potassium . . .	10.33	10.41	10.24	9.43
Lead	32.05	31.90	32.49	33.30
Bromine . . .	51.96	52.15	52.05	51.48
Water		5.59	5.28	5.79
		100.05	100.06	100.00

The analyses agree with the formula as well as could be expected, considering the instability of the compound. The

analyses show, almost exactly, one atom of extra bromine for two atoms of lead, so that the compound is closely related to the iodide, if not exactly analogous to it.

The satisfactory crystals of the bromide, and the stability of the iodide, suggested the possibility that, if the two compounds were really analogous, as suspected, isomorphous mixtures of the two could be made which would retain the desirable qualities of both, so as to be solidly crystallized and stable enough to be accurately analyzed. Experiments showed that isomorphous mixtures could be readily obtained which crystallized satisfactorily, and it was found that even small amounts of iodine had the effect of greatly increasing the stability of the compound. It was noticed that when a product was made from a solution containing free bromine and iodine in nearly atomic proportions (BrI), an almost perfectly stable, bright red salt was obtained. The color of this salt is far from being intermediate between that of the black iodide and the dark brown bromide, but, since the analyzed products contain about 23 atoms of bromine to one of iodine, it does not seem probable that any definite relation between the two halogens exists. It is remarkable that such a small proportion of iodine should have so great an influence upon the color and stability of the product, but it is to be noticed that only one-eighth of the halogens in these compounds is in excess, so that, if all the iodine is in this condition, it amounts to about one-third of this excess.

The crops A and B had a dark bronze color. They were successive crops, made by adding bromine to a strong solution of potassium iodide containing lead iodide. The exact conditions are unknown, but it is probable that insufficient bromine was used to set free all the iodine which the solution contained. These products were apparently as stable as the iodide.

C and D were successive crops, made by continuing the addition of bromine to a somewhat similar solution until a change of color showed that the free iodine had been converted into BrI. These salts were red. An analysis of the mother-liquor

from D gave, KBr = 31.3, $PbBr_2$ = 1.8, Br = 6.7, I = 8.3, H_2O (difference) = 51.9.

E was made by adding 31 g. of bromine to 430 g. of the above-mentioned analyzed solution. This crop was also red, but it was not quite as bright in color and not as stable as the others. On continuing the addition of bromine, still less stable crops were obtained, which approached the pure bromide in color. These were not analyzed.

The analyses of the five crops are as follows:

	K.	Pb.	Br.	I.	H_2O.	
A . . .	9.41	31.57	41.40	12.06	5.09 =	99.53
B . . .	9.24	31.55	39.27	14.57	. . .	. . .
C . . .	9.90	32.88	48.66	3.40	5.24 =	100.08
D . . .	9.99	32.74	48.70	3.30	5.02 =	99.75
E . . .	10.24	32.26	49.97	2.07	. . .	. . .

The ratios calculated from the above analyses are as follows:

	K :	Pb :	Br + I :	H_2O.
A	1.57	1.	3.99	1.83
B	1.55	1.	3.99	. . .
C	1.59	1.	4.00	1.82
D	1.61	1.	4.00	1.76
E	1.68	1.	4.16	. . .

The ratio required for the formula $K_8Pb_2(Br,I)_8.4H_2O$ is

K :	Pb :	Br + I	H_2O.
1.50	1.	4.	2.

The analyses agree well with this formula, except that the water is somewhat low. Although $3\frac{1}{2}$ molecules of water would correspond more closely to these analyses than 4, the latter number is considered more probable, on account of the fact that the analyses of the iodide show some excess over four molecules.

It is to be seen that these mixed salts correspond in composition to the bromide. The analogous mode of formation of the iodide, the identical relation of the lead to the extra halogen in the iodide and the other products, as well as the

existence of these mixed salts, make it appear certain that the analyzed iodide was invariably impure, and that the pure compound should be considered as analogous to the other salts. This view has been confirmed by a crystallographic examination of the iodide and the red bromo-iodide, which Prof. S. L. Penfield has kindly undertaken. He has found that both these salts crystallize in prisms of the tetragonal system. Unfortunately the crystals of the iodide were without terminations, so that a more detailed comparison of the two salts could not be made.

The nature of these peculiar salts is not clear. If they are, strictly, hydrous "double salts," such higher halides as Pb_2I_5 or K_3I_4 must be assumed. If they are formed from such compounds as PbI_4 or KI_3, they must be considered as hydrous triple salts.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1893.

ON THALLIUM TRIIODIDE AND ITS RELATION TO THE ALKALI-METAL TRIIODIDES.*

By H. L. WELLS and S. L. PENFIELD.

The well-known resemblance between the thallous salts and many of the corresponding alkali-metal salts has led us to prepare thallium triiodide and to compare its crystalline form with that of the alkali-metal triiodides.† As a result, it has been found that TlI_3 agrees, with remarkable closeness, in form with RbI_3 and CsI_3, and thus a case of isomorphism is established between the higher iodides of thallium and the alkali-metals.

This isomorphism is of special interest because our study of the trihalogen compounds of cæsium has led us to the conclusion that these have the structure of double salts. We consider the evidence of this double-salt structure as very strong, and since it seems necessary to infer that isomorphism indicates the same arrangement of the atoms, we are obliged, in spite of the apparent trivalence of thallium in thallic compounds, to conclude that TlI_3 is also a double salt, to which the formula $TlI.I_2$ should be given. It is not safe to assert at present that all thallic salts must be similarly constituted, for it is possible that thallium triiodide is not a true thallic compound at all, and that thallic sulphate, nitrate, etc., have an entirely different kind of structure. If it is granted that thallium triiodide is a double salt, it seems probable that many other compounds, which are considered as showing higher valence of elements, may, in reality, have the structure of double salts or "addition products."

Thallium triiodide was first described by Nicklès,‡ who prepared it by evaporating an ethereal solution of thallous iodide

* Amer. Jour. Sci., xlvii, June, 1894.

† Ibid., III, xliii, 17 and 475.

‡ J. Pharm. [4], 1, 25.

and iodine. Nicklès states that he did not obtain it in a pure condition, but that his product always contained an excess of iodine. He described its crystalline form, and his results will be mentioned beyond.

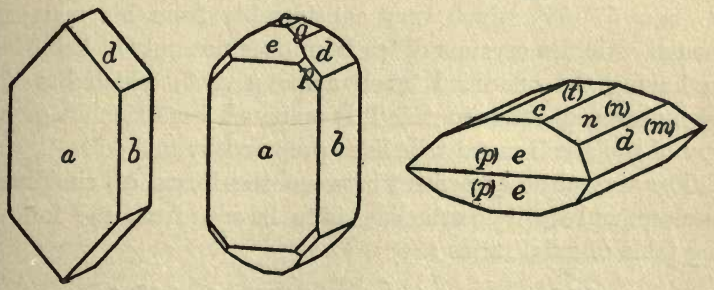
We have modified Nicklès' method by using alcohol as a solvent, and have encountered no difficulty in obtaining a pure product. The amount of iodine used was slightly in excess of the calculated quantity, and the solution, produced after long digestion, was evaporated over sulphuric acid until crystallization took place. The resulting crystals were frequently of large size, perfectly black, with a magnificent lustre which was slowly lost upon exposure. A sample of the salt, simply pressed upon paper, gave the following results upon analysis:

	Found.	Calculated for TlI_3.
Thallium . . .	34.22	34.87
Iodine	64.80	65.13

An examination of the crystals has shown that they are orthorhombic and isomorphous with the orthorhombic alkali-metal trihalides. Moreover, all the forms which have been observed have also been found on the alkali-metal salts, and are as follows:

a, 100, $\dot{\imath}$-$\bar{\imath}$ *c*, 001, *o* *d*, 011, 1-$\breve{\imath}$ *p*, 111, 1
b, 010, $\dot{\imath}$-$\breve{\imath}$ *g*, 012, $\frac{1}{2}$-$\breve{\imath}$ *e*, 102, $\frac{1}{2}$-$\bar{\imath}$

1. 2. 3.



The habit is shown in Figs. 1 and 2, the latter being remarkably like that of CsI_3, when this had been crystallized

from alcohol. The measurements which were chosen as fundamental are $d \wedge d$, $011 \wedge 0\bar{1}1 = 96° 34'$ and $e \wedge e$, $102 \wedge \bar{1}02 = 78° 48'$, giving the axial ratio :

$$\breve{a} : \bar{b} : \dot{c} = 0.6828 : 1 : 1.1217$$

The dome g was determined by the measurement $g \wedge g$, $012 \wedge 0\bar{1}2 = 58° 34'$, calculated $58° 34'$, and the pyramid p by its position in the zones $a - d$ and $d - e$.

A description of this salt, including a figure, has been given by Nicklès. His salt, crystallized from ether, had the habit shown in Fig. 3, the letters in brackets being those used by him and the position being changed to correspond with the orientation of the alkali-metal trihalides. He considered p as a prism, t as a macropinacoid, and m and n as brachydomes. No calculations are given, and only the following four measurements :

Nicklès. Measured.	Calculated from author's measurement.
$p \wedge p = 100° 15'$	$101° 12'$ for $e \wedge e$, $102 \wedge 10\bar{2}$
$p \wedge t = 39° 22'$	$39° 24'$ " $e \wedge c$, $102 \wedge 001$
$p \wedge m = 61°$	$59° 3'$ " $e \wedge d$, $102 \wedge 011$
$n \wedge t = 19° 25'$	$20° 30'$ " $013 \wedge 001$

The agreement between the measured and calculated angles is not very close, but Nicklès' measurements cannot be very exact, for if we take $p \wedge t = 39° 22'$ and $n \wedge t = 19° 25'$ as fundamental, we find by calculation $p \wedge p = 101° 16'$ and $p \wedge m = 57° 55'$, which vary considerably from his measurements. Nicklès crystals differ from ours not only in habit but in having the one-third brachydome n, 013, which has not been observed either in the TlI_3 prepared from alcohol or on any of the alkali-metal trihalides prepared by us.

The very close agreement between the forms of rubidium, cæsium, and thallium triiodides is to be seen from the following table of axial ratios :

RbI_3 . . . $\breve{a} : \bar{b} : \dot{c} = 0.6858 : 1 : 1.1234$
CsI_3 . . . " " " $= 0.6824 : 1 : 1.1051$
TlI_3 . . . " " " $= 0.6828 : 1 : 1.1217$

Our previous observation, that the exchange of one metal for another in the trihalogen compounds usually has little or no effect upon the crystalline form, is strongly confirmed by these ratios, and the remarkable agreement between the rubidium triiodide and the thallium compound is very striking, when the great difference between the atomic weights of the two metals is considered.

It was hoped that a pentaiodide of thallium could be prepared, in order that its form might be compared with that of cæsium pentaiodide, but, by the use of increasing proportions of iodine with thallium triiodide in alcoholic solutions, no evidence of the existence of such a compound could be obtained.

The remarkably close relations of thallium to the alkali-metals, as far as the thallous compounds are concerned, and the additional resemblance which has been pointed out in the present communication, have led us to consider the possibility that thallium has been wrongly placed in the periodic system of the elements and that it really belongs to the alkali-metals. There are two vacancies in Mendeléeff's table in the alkali-metal group corresponding to atomic weights of about 170 and 220. One of these is smaller, the other larger than the accepted atomic weight of thallium, so that, as far as these numbers are concerned, thallium might be composed of two alkali-metal elements. Although the probability that thallium was composed of two elements seemed very slight from other considerations, we have deemed it desirable to test the question experimentally.

About 200 g. of thallium were converted into the nitrate, and this was systematically fractionated by crystallization, until about one-twentieth of the salt remained as a repeatedly recrystallized portion, and about another twentieth was contained in a final mother-liquor. From each of these two fractions, thallous chloride was prepared by converting into sulphate, precipitating impurities with hydrogen sulphide, and finally precipitating thallous chloride by means of hydrochloric acid. The preparations were carefully washed, dried at 100°, and the chlorine was determined as silver chloride in order to

get the atomic weight of the metal in each fraction. The silver chloride was weighed in the Gooch crucible, a method which can be most highly recommended for accurately weighing this substance. The following results were obtained, the weights being given as taken in air:

	Crystallized End. g.	Soluble End. g.
TlCl taken	3.9146	3.3415
AgCl obtained	2.3393	1.9968
Atomic weight of Tl (0 = 16) .	204.5	204.5

It was not expected that absolute accuracy in the atomic weight of thallium would be attained, but since the same method of purification and analysis was used in both cases, the two results are comparable with each other, and their exact agreement shows that the fractionation of the nitrate gives no change in the atomic weight of thallium, and no evidence has been obtained that thallium is not homogeneous.

SHEFFIELD SCIENTIFIC SCHOOL,
January, 1894.

ON SOME COMPOUNDS CONTAINING LEAD AND EXTRA IODINE.*

By H. L. WELLS.

About two years ago, the writer described † the double salts of lead tetrachloride, $(NH_4)_2PbCl_6$, K_2PbCl_6, Rb_2PbCl_6, and Cs_2PbCl_6, and upon attempting to prepare the corresponding bromides and iodides, an entirely different kind of double salts was discovered.‡ These peculiar salts were $K_3Pb_2Br_8.4H_2O$ and $K_3Pb_2I_8.4H_2O$. They are remarkable in containing but a single atom of extra halogen in the formula as given above, and they apparently correspond to no previously known compound. I was unable to obtain, with the alkali metals, any bromides or iodides corresponding to the chlorides, but it is interesting to notice that Classen and Zahorski § have obtained such salts with quinoline, $(C_9H_7NH)_2Pb_6Br_6$ and $(C_9H_7NH)_2PbI_6$.‖

The isolation of lead tetrachloride by Friedrich,¶ and the discovery of lead tetraacetate, $Pb(CH_3CO_2)_4$, by Hutchinson and Pollard,** were very interesting additions to our knowledge of the compounds of tetravalent lead. These articles appeared almost simultaneously with that of Classen and Zahorski, which has been referred to above, and with my own work mentioned at the beginning of this article.

As a sequence to my former investigations, it has seemed to be desirable to reinvestigate two previously described compounds containing lead and extra iodine, because it seemed

* Amer. Jour. Sci., l, July, 1895.

† Ibid., xlvi, 180, 1893. ‡ Ibid., 190, 1893.

§ Zeitschr. für anorg. Chem., iv, 107, 1893.

‖ Classen and Zahorski gave a formula of different type, $5NH_4Cl.2PbCl_4$, to the double ammonium chloride. It seems certain from analogy, from Friedrich's results, and from my own work, that their product was contaminated with ammonium chloride.

¶ Berichte, xxvi, 1434, 1893. ** Chem. Soc. Jour., lxiii, 1136, 1893.

possible that a further study of them might throw some light upon the nature of the curious salt, $K_3Pb_2I_8.4H_2O$.

Johnson's Salt. — By mixing a hot, concentrated alcoholic solution of potassium triiodide with a saturated solution of lead acetate in boiling alcohol, filtering off the small precipitate thus produced, and cooling, G. S. Johnson * obtained a crystalline substance to which he gave the formula, $Pb_8C_{36}H_{54}O_{28}K_6I_{17}$. Concerning this he remarks, "The formation of a *rational formula* has at present baffled all my endeavors."

Johnson also obtained the salt by recrystallization from alcohol and by evaporating the mother-liquor over sulphuric acid, but there is no evidence that he analyzed more than one sample of it. He does not give the quantities used in making his preparation.

I have made a large number of crops of the compound, all of which agreed with Johnson's description in forming rectangular crystals, of a black color, having a marked brassy lustre upon four of the six faces, and occurring usually in intergrown groups of nearly square, flat plates. In preparing these products the conditions were varied considerably. As a starting-point 30 g. of potassium iodide and 50 g. of iodine were invariably used. These amounts give a slight excess of iodine over the proportion required for potassium triiodide. From 40 to 100 g. of crystallized lead acetate were used, and it was found that beyond these limits the preparation was unsuccessful.

The solvent varied from absolute alcohol, diluted only with the water of crystallization of the lead acetate, to alcohol diluted with one-half its volume of water. Several crops were prepared in the presence of glacial acetic acid, and a volume of this amounting to $\frac{1}{15}$ of the total liquid (20 c. c.) was used with success. The total volume of solvent varied from 200 to 500 c. c., the larger amounts being used when it was not expected to obtain the product by simple cooling. It was customary to dissolve the potassium iodide and iodine in about one-half of the solvent to be used and the lead acetate in the remainder. The solutions were sometimes mixed boiling hot, while at

* Chem. Soc. Jour., xxxiii, 189, 1878.

other times a lower temperature was employed. A precipitate, evidently consisting chiefly of lead iodide, was always produced by mixing the two liquids, but its quantity was usually small. The effect of the presence of iodine in preventing the precipitation of lead iodide to a great extent is very remarkable. The solutions were filtered, sometimes while hot, sometimes after a longer or shorter period. The products obtained by cooling formed coherent crusts composed of very small, intergrown crystals, while by evaporation over sulphuric acid much larger isolated crystals, or groups of crystals, were deposited. All the analyses given below were made upon crops obtained by evaporation, except in one instance. Two partial analyses of products made by cooling are not included in the list, because the results varied rather widely from each other and from the results obtained with the products of evaporations. The omitted results differed still more from Johnson's analysis than the others. Two or three successive crops were often obtained by evaporating a single solution, and the twelve products, analyses of which are given, represent six different original solutions. The products were well crystallized and most of them seemed entirely satisfactory in regard to purity. They were all examined microscopically, and as far as could be judged from the appearance of an opaque substance, no impurities were present. The samples for analysis were very carefully pressed upon filter-paper in order to remove the mother-liquor. The salt is practically stable in the air, so that decomposition was not to be feared during the drying operation.

Lead and potassium were determined by dissolving the substance in dilute nitric acid, evaporating with sulphuric acid, separating the lead sulphate by filtration, weighing it, and determining potassium in the filtrate by weighing it as sulphate. Iodine was determined by treating the substance with a solution of sodium arsenite, acidifying with nitric acid, digesting with an excess of silver nitrate, and finally weighing silver iodide. Carbon and hydrogen were determined by combustion with lead chromate, where the front part of the tube contained a layer of metallic silver which stopped the passage of any iodine.

The variations in the results of the analyses are considerable, and it is probable that the salt, being always deposited in a concentrated mother-liquor, was never quite pure, but there is no evidence that the variations in composition have been regularly influenced by the variations in the conditions of preparation. The analyses are given in the order in which they were made. The last three probably represent better material than the others.

	Lead.	Potassium.	Iodine.	Carbon.	Hydrogen.	Oxygen (difference.)
I	35.51	4.01	37.50	. . .	. . .	. . .
II	36.24	4.33	36.16	. . .	. . .	. . .
III	35.83	4.32	36.01	. . .	. . .	. . .
IV	35.29	4.07	37.78	. . .	. . .	. . .
V	36.21	4.59	. . .	. . .	. . .	. . .
VI	35.43	4.20	. . .	. . .	. . .	. . .
VII	35.65	4.40	36.49	. . .	. . .	. . .
VIII	35.35	4.15	. . .	. . .	. . .	. . .
IX	34.80	4.42	. . .	. . .	. . .	. . .
X	34.85	3.93	37.92	9.14	1.39	12.77
XI	34.72	3.97	39.26	9.17	1.41	11.47
XII	34.33	3.94	39.83	8.77	1.31	11.82
Calculated for $5Pb(CH_3CO_2)_2.3KI.6I$,						
	35.87	4.07	39.62	8.31	1.04	11.09
Johnson found,						
	33.195	4.668	43.37	8.63	1.106	9.031

It must be admitted that the results do not agree very satisfactorily with the calculated quantities, and that the formula is somewhat uncertain. It seems probable, however, that the compound is a combination of lead acetate with potassium triiodide with the formula $5Pb(CH_3CO_2)_2.3KI_3$. It is not certain that the extra iodine is combined with the potassium rather than with the lead, but since KI_3 is a well-known compound, and since the acetic acid radical is present in the proper proportion to form lead acetate, this view seems to be the most plausible one.

Johnson's analysis differs chiefly from the new ones in its higher iodine and consequently lower oxygen as determined by difference. His oxygen is considerably too low for the amount required to give CH_3CO_2 with the carbon and hydrogen, and this was evidently the main cause of his inability to arrive at a rational formula. It seems probable that there was an error in his determination of iodine.

Gröger's Salt. — A compound has been described by Max Gröger * as corresponding to the remarkable formula, $PbO.PbI_2.I_8$. As he prepared it, it was an amorphous precipitate which had been washed with water, and exposed to the air for a long time in order to allow iodine with which it was mixed to evaporate, and, consequently, there seemed to be room for doubt as to its freedom from decomposition after it had undergone these operations, even if it could be supposed to have been a pure substance when it was precipitated.

I have undertaken a reinvestigation of this salt, and have succeeded in preparing it in a beautifully crystalline condition in which there was no doubt about its purity, and have found that Gröger really analyzed a pure compound, but that he overlooked some water that it contained. With the addition of one molecule of water his formula becomes correct, but this formula, $Pb_2I_5O.H_2O$, or, as it may be written, $Pb_2I_5(OH)_2$, is no less remarkable than the one which Gröger advanced.

This substance, in a crystallized condition, had been observed in this laboratory a short time before Gröger's work was known here. At my suggestion, Mr. J. H. Pratt had made some experiments with the dark-colored precipitate produced by mixing strong aqueous solutions of lead acetate and potassium triiodide. Such precipitates were collected upon filters, treated while still moist with boiling alcohol, and the resulting liquid, after filtration, was evaporated over sulphuric acid, with the result that small, brilliant black crystals were sometimes obtained. Several partial analyses of this substance showed that it contained lead and iodine in the ratio 2 : 5, and were as follows:

* Monatshefte für Chemie, xiii, 510, 1892.

	I.	II.	III.	Ratio of average.	Calculated for $Pb_2I_2O.H_2O$.
Lead . . .	37.84	. . .	37.32	2.00	38.23
Iodine . .	57.66	58.71	58.62	5.07	58.63

The yield of this product was very small, and it was difficult to obtain it in a pure condition, since it was often mixed with the well-known compound PbIOH, and with other substances which were not identified. The presence of water in the salt was established, but the circumstances were such that the investigation was interrupted at a point where the pure material at hand had been exhausted, and no accurate determination of water had been made.

My thanks are due to Mr. Pratt for his valuable assistance in the investigation of the compound up to this point. When I subsequently obtained Gröger's salt in a crystallized condition, it proved to have the same form and composition as the product mentioned above, so that a further study of the latter was deemed unnecessary.

In order to obtain Gröger's compound in a well-crystallized condition, it is necessary to modify his method of preparation by using a small amount of acetic acid. It is also advantageous to use boiling water instead of cold water for the precipitation, and to use a somewhat larger volume of this than is recommended by him. I have obtained the best results by the following method: Dissolve 10 g. iodine in 100 c.c. absolute alcohol, then 50 g. crystallized lead acetate in 150 c.c. water, 3 c.c. glacial acetic acid, and 300 c.c. absolute alcohol. Mix the two solutions, let stand 14 to 16 hours at the temperature of the room, filter to remove the small precipitate, then dilute with 1500 c.c. of boiling water. Let the whole stand until cold, when the compound sought will have crystallized out mixed with iodine. Pour off the liquid and wash the crystals with cold alcohol in small quantities until the iodine is removed. Dry the product upon filter-paper, and then in the air at ordinary temperature.

The product consists of very brilliant black crystals, usually 0.5 mm. or less in diameter. They form octahedra, appar-

ently of the tetragonal system, with faces that are much curved and otherwise distorted. The powder of the crystals is similar in color to Gröger's precipitate, and it agrees with it in being practically stable in the air and scarcely acted upon by cold water or alcohol.

Two separate crops of apparently perfect purity were analyzed. Lead and iodine were determined by the methods described above under Johnson's compound. Water was collected and weighed in a calcium chloride tube, the substance being ignited in a tube behind a layer of granulated sodium carbonate which held back the iodine completely. Free iodine was determined volumetrically by the use of sodium thiosulphate solution. The results were as follows:

	Found. I.	Found. II.	Calculated for $Pb_2I_5(OH)_3$.
Lead	38.54	38.22	38.23
Iodine	58.41	58.62	58.63
Water	1.83	1.82	1.66
Oxygen (diff.) . .	1.42	1.34	1.48
	100.00	100.00	100.00

"Free" iodine . . .	34.78	. . .	I_3	35.18
Loss by heating . . .	36.43	36.43	$I_3 + H_2O$	36.84

I have also prepared the compound, exactly according to Gröger's directions, as a reddish-brown precipitate, and after the product was apparently free from intermixed iodine and air-dry, it was dried for three days, spread out in a very thin layer under a bell-jar well charged with solid potassium hydroxide. This product gave the following results on analysis:

	Found.	Calculated for $Pb_2I_5(OH)_3$.
Water . . .	1.80	1.66

This result indicates that Gröger overlooked water in his compound, and that his precipitate is identical with the crystallized product.

I have observed the formation of this salt, under various conditions, when alcoholic solutions containing lead acetate and

iodine, and in some cases potassium iodide also, were diluted, but the purest crops have been obtained only when the ingredients were used nearly in the proportion which Gröger recommends, and also when the alcoholic mixture has been allowed to stand for the proper period. The compound cannot be recrystallized from water, alcohol, or mixtures of the two liquids, and it seems probable, as Gröger suggests, that it is formed by the decomposition of some other compound by water. This view does not conflict with the fact that it was prepared, as described above, by the evaporation of certain alcoholic solutions, because these always contained water which increased in proportion to the alcohol as the evaporation went on. The presence of an acetate seems to be indispensable to its production, for I have made a number of experiments using lead nitrate instead of the acetate with no indication of its formation. It seems probable that a soluble compound closely related to Johnson's salt is formed at first, and that this yields Gröger's compound by the action of water.

I have made unsuccessful attempts to prepare a bromide corresponding to Gröger's salt, and my attempts to replace a part of the iodine in it by bromine have also failed.

Conclusion.— The two compounds which have been re-investigated, $5Pb(CH_3CO_2)_2.3KI.6I$ and $PbI_2.PbO.3I.H_2O$, show no evident relation to each other nor to the compound $2PbI_2.3KI.I.4H_2O$, which I have previously described, except that all of them are of complicated composition and they all contain extra iodine without showing evidence of the existence of lead tetraiodide. Classen and Zahorski's quinoline salt, previously referred to, seems to furnish the only evidence of the existence of this higher iodide in combination.

SHEFFIELD SCIENTIFIC SCHOOL,
March, 1895.

ON THE VOLUMETRIC DETERMINATION OF TITANIC ACID AND IRON IN ORES.*

By H. L. WELLS and W. L. MITCHELL.

The difficulties connected with the gravimetric determination of titanic acid make a reliable volumetric method very desirable, especially for the analysis of titanic iron ores. We have therefore turned our attention to this subject, and have found that satisfactory results can be obtained by a slight modification of a process which has long been known.

About thirty years ago F. Pisani† stated that the acid under consideration could be determined by reduction with zinc in hydrochloric acid solution, using a gentle heat, and when the violet color no longer deepened, pouring off the liquid from the remaining zinc and titrating with potassium permanganate. Pisani gave no test analyses, and, since his process has not been generally adopted, it is evident that it has not proved satisfactory in the hands of others.

A number of years ago one of us (Wells) had occasion to analyze a large number of titanic iron ores, and attempted to use Pisani's method with the use of sulphuric acid instead of hydrochloric acid, as recommended by the originator of the process. This modification was made on account of the well-known interference of chlorides with the permanganate method, and it was found that the difficulty mentioned by Pisani, that titanic acid was liable to be precipitated by heating sulphate solutions, could be readily overcome by using a sufficiently large quantity of sulphuric acid. The results of a great many trials at that time, however, showed that the method gave very low results, and the process was then abandoned. The process used in the experiments just referred to was precisely the same

* Jour. Amer. Chem. Soc., xvii, November, 1895.

† Compt. rend., lix, 289.

as that which we now recommend and which will be described in detail below, except that, after reduction with zinc, the solution was poured off from the excess of that metal into a beaker for titration, an operation which Pisani recommended, and which is customary in the determination of iron by this method. It is now evident that the failure of the method was due to the contact of the solutions with atmospheric air, for, while ferrous sulphate is acted upon very slowly, the sulphate corresponding to the lower oxide of titanium is very rapidly oxidized under such circumstances.

Marignac,* with his accustomed skill, applied Pisani's method, soon after its publication, to the determination of titanic acid in the presence of niobic acid. He was obliged to use special conditions in order to avoid the reduction of the other acid at the same time, but the feature of his process which is interesting in the present connection is, that he reduced the titanic acid by means of a long rod of pure zinc extending up into the neck of the flask which held the solution, and, after allowing the reduction to take place out of contact with air, he finally took out the zinc and titrated directly in the flask without transferring. Marignac gave a number of test analyses which showed that the method gave very good results, although they were a little too low with the larger quantities of titanic acid used.

We have modified the method of Pisani, as improved by Marignac, by using sulphuric acid solutions and by protecting the liquid during cooling and titration by means of carbon dioxide, and we have also arranged the process for the determination of iron along with the titanic acid. The details of the operation are as follows:

Five grams of very finely pulverized ore are placed in a rather large beaker, covered with a watch-glass, and treated with about 100 c. c. of concentrated hydrochloric acid. A very gentle, gradually increasing heat is applied for several hours, more hydrochloric acid is added if necessary, and, when no further action is apparent, about 50 c. c. of a mixture of equal volumes

* Zeitschr. anal. Chem., vii, 112.

of concentrated sulphuric acid and water are added, and the whole is evaporated until the sulphuric acid fumes strongly. After cooling, about 200 c. c. of water are added, the whole is heated until the sulphates are dissolved, and the liquid is filtered into a liter flask. With many titanic ores this operation will have dissolved everything except siliceous matter. If, however, some undissolved ore remains, it is ignited, to burn the filter-paper, in a platinum crucible, and the residue is fused with potassium disulphate, at a gradually increasing heat, up to low redness, until the black particles have disappeared. To the cake in the crucible several volumes of concentrated sulphuric acid are added, heat is gradually applied until the whole becomes liquid, then this is heated with a moderate volume of water to dissolve the sulphates, and the liquid is added to the main solution in the liter flask. Filtration may be omitted here, or in the case of the original solution, provided that the siliceous matter is not to be weighed.

The liquid in the liter flask is diluted to the mark and mixed, and four portions of 200 c. c. each, representing 1 g. of ore, are taken, two of them into Erlenmeyer (conical) flasks of 500 c. c. capacity, and the other two into ordinary flasks of 350 c. c. capacity.

To determine iron, hydrogen sulphide is passed into the solutions in the ordinary flasks until they are saturated with the gas, then inverted porcelain crucible covers are placed upon the mouths of the flasks, and the solutions are heated and boiled continuously, so that air cannot enter, until the hydrogen sulphide has been completely removed. This point can be determined by testing the escaping steam with paper which has been dipped in a solution of lead acetate made strongly alkaline with potassium hydroxide. The flasks are then quickly filled to the neck with cold distilled water (which has been recently boiled), best by means of an inverted wash-bottle, directing the stream against the neck of the flask in such a way that the water does not mix to a great extent with the heavier sulphuric acid solution. If the stream of cold water does not strike the top of the neck, there is little danger of

breaking the hot glass. The contents of the flasks are now rapidly cooled by means of a stream of water, transferred to large beakers, and titrated with potassium permanganate solution.

To the solutions in the Erlenmeyer flasks, about 25 c. c. of concentrated sulphuric acid are added, then, in each case, three or four rods of chemically pure zinc, about 50 mm. long and 6 or 7 mm. in diameter, are attached to the loop of a porcelain crucible cover, which is larger than the mouth of the flask, by means of platinum wire wound securely around them near the middle. The length of the wire is so arranged that the pieces of zinc will be suspended in the liquid when the cover is placed on the flask. When this has been accomplished, the liquid is boiled gently, so as to keep out air, for thirty or forty minutes, then, without interrupting the boiling, a glass tube, so bent that it extends 50 mm. or more into the flask, and which is delivering a rather rapid stream of carbon dioxide, is introduced under the cover. Care should be taken to have the carbon dioxide free from air, and that hydrochloric acid which contains sulphur dioxide is not used for its generation. The flask is now rapidly cooled, and then the zinc is washed with a jet of water and removed, and the solution is titrated with permanganate in the flask while the carbon dioxide is still being passed in. The difference between the permanganate used in this case and that used for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0.7 gives the factor for titanic acid (TiO_2).

When a 50 c. c. burette is used, the most convenient strength for the permanganate solution is when 1 c. c. is equal to about 0.014 g. of metallic iron, corresponding to 7.9 g. of potassium permanganate per liter.

It is customary in this laboratory to standardize permanganate solutions by a method which very closely approaches the one described above for the actual determination of iron, so that, if any slight errors are inherent in the process, they are likely to be eliminated because they have an equal effect upon

the standardization and the determination. The method is simple and convenient, and a large amount of experience has shown it to be very accurate. To carry out this operation, a 350 c. c. flask is half filled with sulphuric acid (the strong acid diluted with about eight volumes of water). This is heated to boiling with an inverted crucible cover upon the mouth of the flask, and, after the air had been expelled, about 0.6 g. of the purest iron wire, representing nearly the average amount of iron in 1 g. of an ore, is dropped in, and gentle boiling is continued until it has dissolved. The flask is filled to the neck with water, cooled, and finally the liquid is transferred to a beaker and titrated.

The method of determining iron by reduction with hydrogen sulphide, although well known, does not appear to be as generally used as it deserves to be. The precipitated sulphur present in the liquid has absolutely no effect upon cold permanganate solution, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling. Since concentrated sulphuric acid is an oxidizing agent, care must be taken to use sufficiently dilute solutions, and not boil them down until the acid becomes strong.

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.7638	0.1437	0.1527	—0.0090
0.6425	0.1225	0.1285	—0.0060
0.7778	0.1524	0.1555	—0.0031
0.6793	0.1308	0.1358	—0.0050
0.8226	0.1607	0.1645	—0.0038
1.0956	0.2107	0.2191	—0.0084
0.4451	0.0848	0.0890	—0.0042
0.6359	0.1215	0.1271	—0.0056
0.9004	0.1715	0.1800	—0.0085
0.4634	0.0882	0.0926	—0.0044

We have made some test analyses upon the method of determining titanic acid volumetrically. Crude potassium titanofluoride, K_2TiF_6, was recrystallized twice from water and used as the source of titanium. Weighed quantities of the care-

fully dried salt were evaporated with sulphuric acid, and the resulting substance was treated essentially as has been described above, but with some variations in the time of boiling, the strength of the acid, and the amount of zinc used. The table on page 101 gives the results obtained in grams.

The results show a fair degree of uniformity, but they are invariably too low. A part of the deficiency was probably due to the impurities in the potassium titanofluoride used, for it is quite possible that certain impurities may have been increased rather than diminished by recrystallizing it, and it is exceedingly difficult to obtain any titanium compound that is certainly free from all other acid-forming elements. The greater portion of the error was doubtless due to the action of air which gained access to the liquid in spite of the precautions used, and it is evident that the accuracy of determinations made by this method would be increased by adding one-twentieth or one-thirtieth to the amount of titanic acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the preceding table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric determination, unless great care and skill are displayed in carrying out the latter.

SHEFFIELD SCIENTIFIC SCHOOL,
October, 1895.

ON SOME COMPOUNDS OF TRIVALENT VANADIUM.*

By JAMES LOCKE and GASTON H. EDWARDS.

The green solution obtained when vanadic acid is reduced by nascent hydrogen has been but very slightly studied. That it contains salts of vanadium in the trivalent state was recognized by Roscoe† in the course of his elaborate investigation on the chemical nature of this element. Roscoe, however, made no attempt to study the products which could be obtained from the solution which he prepared by dissolving the anhydrous chloride, VCl_3, in water, and failed to make any comparison between that body and the chlorides of other trivalent elements.

The first compounds to be isolated from a vanadic solution were prepared by Petersen,‡ who examined in a very thorough manner the fluoride and its double salts with the fluorides of other metals. His results pointed to a close resemblance between vanadium sesquioxide and its derivatives and the compounds of the groups formed by aluminium, chromium manganese, and iron. Thus, the compound $K_2VF_5.H_2O$ exhibits in its general properties, solubility, etc., close similarity to the analogously constituted salts of aluminium, iron, chromium, and manganese. Ammonium vanadifluoride, $(NH_4)_3VF_6$, is isomorphous with the ferric salt, $(NH_4)_3FeF_6$, described by Marignac,§ and Petersen prepared other members of the series in $(NH_4)_3CrF_6$ and $(NH_4)_3AlF_6$. A similar relation was observed between double salts with the fluorides of divalent metals, such as $CoVF_5.7H_2O$, $CoCrF_5.7H_2O$, etc.

* Amer. Chem. Jour., xx, July, 1898.

† Ann. Chem. (Liebig), Suppl., vii, 78.

‡ J. prakt. Chem. (2), xl, 44 (1889). § Ann. chim. phys., (3) lx, 306.

Petersen's work and the conclusions drawn from his results were further substantiated by the recent investigations of Piccini* on the alums of vanadium. He succeeded in isolating the salts $NaV(SO_4)_2.12H_2O$, $KV(SO_4)_2.12H_2O$, $NH_4V(SO_4)_2.12H_2O$, $RbV(SO_4)_2.12H_2O$, $CsV(SO_4)_2.12H_2O$, and $TlVSO_{42}.12H_2O$. With the exception of a short article by Brierly,† who prepared a vanadium sulphuric acid, or 'alum acid,'‡ $V(SO_4)SO_4H.4H_2O$, the above investigations embrace practically all that has been published on vanadic salts.

We have recently undertaken the preparation of a number of other compounds, the analogues of which are of characteristic nature in the case of chromium, in the hope of ascertaining more definitely the influence which the atomic weight of vanadium exerts upon the development of the properties common to the compounds of the group: aluminium, vanadium, chromium, manganese, iron, and cobalt.

The chief difficulty which an investigation of this kind presents lies in the extreme readiness with which vanadic solutions absorb oxygen, with formation of vanadyl salts. Petersen was able to start directly from the anhydrous sesquioxide, which is soluble in hydrofluoric acid. The solutions of vanadic sulphate used by Piccini in the preparation of the alums were obtained simply by the electrolysis of vanadic acid in a solution of sulphuric acid. These methods, while satisfactory in individual cases, are of course limited in their applicability, and they could not be used in the preparation of such compounds as a vanadicyanide, sulphocyanate, or the like. We were therefore compelled to start out from the readily oxidizable vanadic hydroxide, precipitated by an alkali after the reduction of the pentoxide with sodium amalgam.

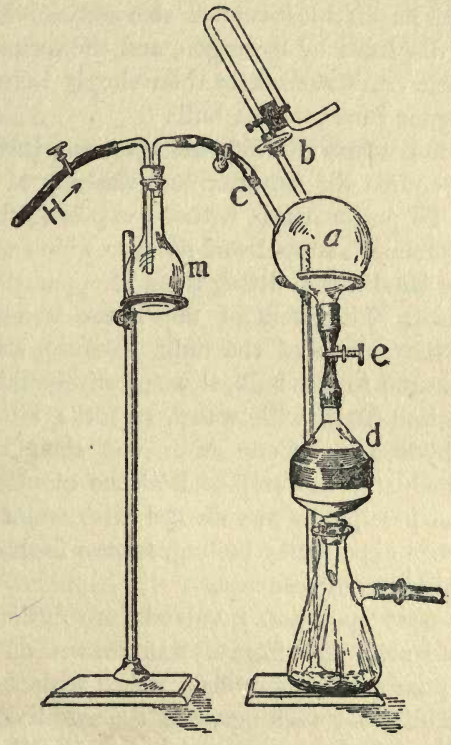
In order to protect the hydroxide and solutions from oxidation, all operations were carried out in an atmosphere of hydrogen. For this purpose the apparatus shown in the

* Zeitschr. anorg. Chem., xi, 106; xiii, 441.

† J. Chem. Soc. (London), xlix, 822.

‡ Chromium is the only other alum-forming metal which yields such an acid, $Cr(SO_4)SO_4H$.

accompanying figure was employed. The pear-shaped bulb *a*, of which we had several pieces, holds about 500 c. c. Over



its drawn-out end, which is two-thirds of an inch in diameter, passes a piece of thick-walled, soft-rubber tubing, which can be closed by a stop-cock *e*. The tube *b* is of capillary diameter, fitted with a glass cock, and bent over on itself, to more securely prevent the entrance of air when this cock is open. *c* is a somewhat wider tube, which serves for the introduction of reagents, and is closed by a stop-cock when necessary.

For heating on the water-bath, the bulb is placed on the latter, mouth downward, while a rapid current of hydrogen is passed in at *c*, *a* being open. The contents of the bulb may be boiled in a similar manner, the bulb then resting on its

side. Reagents are added by means of a small flask *m*, fitted with a cork holding two short tubes, one of which is connected with the hydrogen generator. The reagent having been introduced into the flask (a test-tube is also convenient) the air in the latter is displaced by hydrogen, and the second tube then connected with *c*. The flask is then simply inverted, whereupon the reagent runs into the bulb.

The most important and difficult operation involved in the work was of course the filtration and washing of the vanadic hydroxide. To perform this without exposing the substance to the air, a Buchner's funnel was used, to which was joined by a wide rubber band a well-fitting piece of apparatus, *d*, like an inverted funnel. The stem of the latter was of the same diameter as the mouth of the bulb. Before attaching this filtering-apparatus to the bulb, it was entirely filled, together with the suction-flask, with water, and the latter then displaced by hydrogen. Connection was then made, slight suction applied, and the stop-cock at the mouth of the bulb opened. The precipitate was washed with water from which the air had been expelled by boiling, from a flask connected as for the introduction of reagents.

When the next operation involved the solution of the precipitate in an acid, the filtrate was drawn off by suction through the pump, the suction-flask rinsed with the water from one or two additional washings, and the acid then introduced as above. The solution was then transferred, either to another bulb, or, if it was to be evaporated to crystallization, to a crystallizing-dish, the side tube of the suction-flask being in that case held below the surface of some benzine placed in the dish.

By taking proper care in the observance of minor details, such as the filling of the tubes with water before making connections, etc., we were able almost entirely to obviate the danger of oxidation; and after a little practice we could carry out the operations of filtration and the like almost as rapidly as in the open air. In one afternoon, starting out with vanadium pentoxide, we have prepared vanadium dihydroxide, $V(OH)_2$,

washed it, redissolved in hydrochloric acid, and brought the solution into a desiccator. In spite of all the operations subsequent to the reduction of the vanadic acid, the final solution possessed the true lavender color of vanadious salts, without a trace of green or brown. Roscoe describes such a solution as being a more sensitive reagent towards oxygen than is pyrogallol itself.

The vanadium preparations which we used in this work were placed at our disposal through the kindness of Prof. Paul Jannasch, of Heidelberg, Germany. They consisted chiefly of thoroughly purified vanadates of sodium and ammonium. These compounds were worked up as follows: Enough of the substance to yield about 5 g. of vanadium hydroxide was dissolved in a small quantity of water, 10 c. c. of concentrated hydrochloric acid were added, and the solution boiled with alcohol to reduce the vanadic acid to vanadyl dichloride, $VOCl_2$. After the alcohol had been driven off, the solution was transferred to a bulb, and while a rapid current of hydrogen was led through the latter, 5 per cent sodium amalgam was gradually introduced in small lumps, the solution being in the meantime kept acid by the occasional addition of hydrochloric acid. The reduction was continued until the solution just began to lose the pure green color of the vanadic salts and assume a bluish-green tint, due to compounds of the next lower degree of oxidation. The operation required the addition of about 700 g. of amalgam.

The mercury was next drawn off, the solution filtered, transferred to another bulb, and treated in the cold with just enough ammonium hydroxide to precipitate the vanadic hydroxide * completely. The latter comes down as a dirty green flocculent precipitate, which absorbs oxygen with the greatest avidity. It was allowed to stand for some time, and then filtered and washed thoroughly with warm water from which the air had been expelled. From this precipitate the following salts were obtained by solution and crystallization.

* Potassium hydroxide does not work as well for this purpose, as it dissolves more or less of the vanadic hydroxide.

Vanadium Trichloride, $VCl_3.6H_2O$. — Halberstadt* mentions the fact that when the anhydrous chloride, VCl_3, is dissolved in water and the solution evaporated over sulphuric acid, a very unstable crystalline compound is obtained. Piccini mentions in a foot-note to his first article on the vanadium alums † that he had obtained this substance in distinct crystals, and found it to have the above composition. This foot-note escaped our notice when first reading his article, and at the time of preparing the compound we supposed we were the first to have isolated it. As, however, nearly three years have elapsed since his article was sent in for publication, we may be allowed to describe the compound, yielding to him the priority of its discovery.

It is obtained by dissolving vanadic hydroxide in concentrated hydrochloric acid and evaporating the green solution to dryness in a vacuum-desiccator. The salt separates out from the syrupy liquid in large green prisms, some of which attained with us the length of nearly half a centimeter. It dissolves in water with extreme readiness, yielding, like the other neutral vanadic salts, a brown solution which becomes green on acidification. The salt is very deliquescent, and on exposure to the air for any length of time, dissolves in the water absorbed and is oxidized to vanadyl dichloride. It is readily soluble in both alcohol and ether, but no distinct crystals could be obtained from its solution in these liquids.

In the analysis of the substance the solution was acidified with nitric acid and the chlorine precipitated with silver nitrate. The vanadium was determined in another portion by titration from the tetravalent to the pentavalent state with iodine, according to Browning's ‡ method. The water was estimated by difference: —

	Calculated for $VCl_3.6H_2O$.	Found.
V	19.24	18.96
Cl	40.10	39.95
H_2O	40.66	41.09
	100.00	100.00

* Ber. d. chem. Ges., xv, 1619 (1882).

† Zeitschr. anorg. Chem., xi, 107 (1896).

‡ Ibid., i, 158.

An attempt was made to measure the crystals, but they proved too hygroscopic. Their optical properties, however, were found to conform to the rhombic system. Salts of composition similar to that of this compound are seen in $AlCl_3.6H_2O$, $CrCl_3.6H_2O$, and $FeCl_3.6H_2O$.

Potassium Vanadichloride. — An attempt was made to prepare from the chloride a double salt analogous to those of the series $R_2FeCl_5.H_2O$, in which R is K, Rb, NH_4, etc. A few grams of the trichloride were dissolved in concentrated hydrochloric acid, the calculated quantity of potassium chloride added, and the mixture left to crystallize in a vacuum. The product consisted chiefly of green crystals of a somewhat lighter shade than that of the pure vanadium chloride, but it was impossible to isolate these completely. A vanadium determination, made in as pure a product as we could obtain, showed that it contained 22.41 per cent V. The quantity calculated for the anhydrous compound $KVCl_4$ is 22.03 per cent V.

Vanadium Bromide, $VBr_3.6H_2O$. — This compound was prepared in a manner strictly analogous to that by which the chloride was obtained, pure concentrated hydrobromic acid being used. It crystallizes with less readiness than the chloride, and decomposes more easily. In other respects the two compounds were closely similar. The bromide decomposes more or less on solution in water, leaving as a residue a small quantity of a brown substance, probably a basic bromide. Like the chloride, it is soluble in both alcohol and ether, to a green solution. The analysis was carried out as in the case of the chloride.

	Calculated for $VBr_3 + 6H_2O$.	Found.
V	12.83	12.62
Br	60.10	59.65
H_2O	27.07	27.73
	100.00	100.00

The iodide could not be obtained. Vanadium hydroxide dissolves in hydriodic acid as readily as in hydrochloric or hydrobromic, but the solution turns brown on evaporation

and eventually leaves only an amorphous, brownish-black residue, only partially soluble in water.

Potassium Vanadicyanide, $K_3V(CN)_6$.— For the preparation of this compound, it was found more convenient to start out from the anhydrous vanadium trichloride, which we prepared according to the method of Halberstadt.* About 5 g. of this substance were dissolved in as little water as possible † and slightly acidified with hydrochloric acid. A concentrated solution of potassium cyanide containing about one and a half times the calculated quantity of the salt was placed in a bulb, and the vanadium chloride solution then added. The mixture at once assumed the form of a thick, deep-purple paste which gradually became thin again, though without at first losing its color, and remaining almost opaque. This part of the reaction was observed by Petersen,‡ who states that he thus obtained a dark blue solution. The blue color, however, is in fact due only to very finely divided particles of the original precipitate suspended in the solution, which is itself of a deep wine color. After shaking for some time, the liquid cleared, and only a few flakes of a brown residue, presumably the hydroxide, remained undissolved. It is absolutely necessary to have a considerable excess of potassium cyanide present, as the precipitate dissolves with great difficulty, and a clear solution cannot otherwise be obtained.

The wine-colored solution, after being filtered, was treated with just enough alcohol to bring about incipient precipitation, and then allowed to stand for some hours surrounded by ice-water. A fine precipitate separated out, which consisted of a mixture of potassium cyanide and vanadicyanide, and in addition to this, comparatively large crystals of the latter collected on the sides and bottom of the vessel. These alone were

* Ber. d. chem. Ges., xv, 1619 (1882).

† The formation of the hydrated chloride is readily seen when a quantity of the anhydrous chloride is added to about its own volume of water. It dissolves with a hissing sound, and, on cooling, the liquid solidifies to a green crystalline mass. On addition of more water, this dissolves to a brown solution.

‡ J. prakt. Chem., xl, 50.

saved, the rest of the product being removed by lixiviation. The crystals were repeatedly washed by decantation with 95 per cent alcohol, and finally with ether, and dried in a vacuum-desiccator.

In the analysis of the product the carbon and nitrogen were determined by combustion. The vanadium was estimated by titration with iodine, and the potassium as sulphate, in a separate portion, after the oxidation of the vanadium to vanadic acid and its removal as lead vanadate.*

	Calculated for $K_3V(CN)_6$.	Found.
V	15.74	15.89
C	22.22	21.80
N	25.93	26.36
K	36.11	36.47
	100.00	100.52

This salt forms another member of the series of complex cyanides of the formula $K_3M(CN)_6$, of which the other members as yet known are $K_3Cr(CN)_6$, $K_3Mn(CN)_6$, $K_3Fe(CN)_6$, $K_3Co(CN)_6$, $K_3Rh(CN)_6$, and $K_3Ir(CN)_6$. The crystals obtained were about a millimeter in length, and of a bright scarlet color. Owing to their instability, it was impossible to measure them, and thus determine whether they were isomorphous with the other members of the series. They appeared under the microscope to be rhombic plates, with well-formed domes and base; in polarized light, however, they showed inclined extinction, and are therefore probably monoclinic like the others. In potassium ferricyanide the angle β is 90° 6′.

Potassium vanadicyanide is readily soluble in water, insoluble in alcohol. Its aqueous solution grows turbid within a few minutes, however, but is much more stable when containing some free potassium cyanide. Even in that case it cannot be kept for any length of time. The freshly-prepared solution is at once decomposed by acids, turning green. It

* Roscoe: Ann. Chem. (Liebig), Suppl., viii, 102.

gives off a slight odor of hydrocyanic acid, as does the solid salt itself. The solution is at first stable toward alkalies in the cold, but on heating or standing for some time the hydroxide separates out.

The solution yields colored precipitates with the neutral solutions of various metals, of which the following are the most distinct:

Ferrous iron	red-brown.
Cadmium	yellow.
Copper	yellow.
Nickel	purple.
Manganese	greenish-yellow.

Silver and mercury salts are reduced by it, with deposition of the metals. None of these precipitates is stable toward acids, and their color soon undergoes a change on standing.

We have made repeated attempts to isolate the purple precipitate which separates on the first addition of potassium cyanide to the vanadic solution, but without success. The compound, probably vanadic cyanide, is extremely unstable, and on drying yields a green or brown amorphous product, which is obviously a mixture.

The vanadicyanides of ammonium and sodium seem to exist only in solution. Vanadium cyanide dissolves in excess of ammonium cyanide or sodium cyanide, to solutions of the same color as that of the potassium salt. No crystalline products, however, could be obtained from either solution, either by evaporation or precipitation with alcohol. When the latter is employed, the compounds decompose at once, with separation of a thick blue paste.

The properties and reactions of potassium vanadicyanide are of special interest in view of the relative stability of the complex cyanides of the other metals of the group. The only stable compounds of trivalent cobalt are those which contain the metal as a constituent of a complex radical, either positive, as in the cobaltiamines, or negative, as in $K_3Co(CN)_6$, $H_3Co(CN)_6$, etc. The corresponding ferric compounds, *in*

comparison with other ferric salts, are somewhat less stable than the cobaltic compounds as compared with simple cobaltic salts. Thus, for example, potassium ferricyanide is less stable, compared with ferric sulphate, than is potassium cobalticyanide, when compared with cobaltic sulphate. The complex manganese derivatives are relatively still less stable. Among the latter is a sodium salt, $Na_3Mn(CN)_6$, but the free acid is unknown. Chromic cyanide yields neither an acid, $H_3Cr(CN)_6$, nor a sodium salt, and ammonium chromicyanide * is very unstable. The chromicyanide solutions, however, are stable towards alkalies even on boiling. In the case of vanadium, neither the sodium nor ammonium salts can be obtained; potassium vanadicyanide is instantly decomposed by acids, with evolution of hydrocyanic acid, and is stable towards alkalies only in the cold. The simple vanadic salts are comparatively stable. Aluminium, which has the lowest atomic weight of all the metals in the group, is precipitated as hydroxide when potassium cyanide is added to its solution, and no cyanogen compounds at all of this metal can be obtained. The tendency to form complex radicals, throughout the entire group, as compared with the tendency to form simple salts, is thus seen steadily to diminish with a decrease in the atomic weights of its members.

Potassium Vanadisulphocyanate, $K_3V(CNS)_6.4H_2O$. — Among the characteristic compounds of trivalent chromium the derivatives of chromic sulphocyanate are very prominent. Potassium chromisulphocyanate, $K_3Cr(CNS)_6.6H_2O$, is almost as stable as the chromicyanide. It is not decomposed by either alkalies or acids in cold solution.† A number of other salts, such as $Ag_3Cr(CNS)_6$, $Ba_3[Cr(CNS)_6]_2$, etc., derivatives of the same acid, $H_3Cr(CNS)_6$, are also known.

We have succeeded in preparing a compound of vanadium analogous to this potassium salt, and find that it corresponds very closely to the latter in its reactions. The method employed was as follows:

An alcoholic solution of potassium sulphocyanate was

* Ann. Chem. (Liebig), iii, 163. † Rösler: Ibid., cxli, 185.

made by fusing sulphur with potassium cyanide,* digesting the product with absolute alcohol, and filtering. To this solution was added somewhat less than the calculated quantity of vanadium chloride, dissolved in a small volume of water. A precipitate of potassium chloride at once appeared, and the solution assumed a deep brown color. After digestion for an hour on the water-bath, the solution was concentrated by evaporation, and then placed in a vacuum-desiccator to crystallize. The first crop of crystals consisted of a mixture of about equal proportions of potassium sulphocyanate and vanadisulphocyanate. This was removed, and the evaporation continued until the solution was of a thick, syrupy consistency. A large quantity of homogeneous, dark-red crystals, almost black, were thus obtained. They were cleaned as thoroughly as possible by pressure between filter paper, washed with ether, and dried in a vacuum. The analysis gave the following results:

	Calculated for $K_3V(CNS)_6.4H_2O$.	Found.
K	19.90	19.52
C	12.24	. . .
N	14.29	14.73
S	32.65	33.23
V	8.68	8.55, 8.22, 8.79
H_2O	12.24	13.09
	100.00	

Potassium vanadisulphocyanate, like the corresponding chromium salt, is extremely soluble in both alcohol and water, but is stable only in presence of an excess of potassium sulphocyanate. The pure salt is decomposed by either solvent, forming a green solution. Crystals mixed with a small quantity of sulphocyanate are very hygroscopic, dissolving in the water absorbed. Toward oxygen the salt is the most stable of any which we have prepared. The vanadium in the radical $V(CNS)_6$ undergoes oxidation only very slowly, and in

* Chem. Zeitung, 1866, 666.

presence of potassium sulphocyanate the solution may be left exposed to the air for some time without losing its characteristic dark-brown color. Alkalies precipitate vanadic hydroxide from the solution only on boiling, but it is at once decomposed by acids.

The preparation of corresponding salts of other metals, such as $Na_3V(CNS)_6$, $Ba_3[V(CNS)_6]_2$, etc., we have not yet attempted, but we hope to do so in the near future. Our investigations on the vanadic compounds in general will be continued.

NEW HAVEN, May, 1898.

ON AN ISOMER OF POTASSIUM FERRICYANIDE.*

By JAMES LOCKE and GASTON H. EDWARDS.

The behavior of potassium ferricyanide toward powerful oxidizing agents has been virtually but once the subject of investigation. In 1869 Städeler,† in support of his theory that the iron in sodium nitroprussiate, $Na_2Fe(CN)_5NO_2$, is tetravalent, sought to obtain the related perferricyanide, $K_2Fe(CN)_6$, by the action of iodine upon the ferricyanide. He thus obtained a greenish-brown, crystalline product, which was apparently too impure for analysis, for he assigned the above formula to it without having quantitative data upon which to base his conclusions. A body having approximately the same characteristics as Städeler's compound was afterward obtained by Bong,‡ by the action of potassium chlorate and sulphuric acid upon the ferricyanide. To this product was likewise assigned the formula $K_2Fe(CN)_6$, but it could be prepared only in admixture with a large percentage of potassium sulphate, and no analysis of it was made. The principal work upon the subject, and the only work in which analytical results were obtained, was performed by Skraup in 1877. The latter, to a certain extent, adopted Bong's method, but he substituted hydrochloric acid for sulphuric, and isolated his reaction-product by repeatedly precipitating the aqueous solution with alcohol. He finally obtained a completely amorphous, black or dark-violet powder, which was intensely hygroscopic and smelled strongly of cyanogen. This body Skraup submitted to thorough analysis, but he was unable to obtain satisfactory results. The percentage of cyanogen fell much below the amount calculated for the compound

* Amer. Chem. Jour., xxi, March, 1899.

† Ann. Chem. (Liebig), cli, 1.

‡ Bull. Soc. Chim. (1875), xxiv, 268.

$K_2Fe(CN)_6$ (about 4.0 per cent). But the iron and potassium, while correspondingly high, were present in the approximate ratio of one to two, and he therefore assumed the body possessed the formula previously suggested by Städeler and Bong.

The details of the method of preparation used by Skraup were briefly as follows: Assuming the reaction to proceed in the simplest manner, viz., according to the equation,

$$6K_3Fe(CN)_6 + KClO_3 + 6HCl = 6K_2Fe(CN)_6 + 7KCl + 3H_2O,$$

he added to the hot solution of 50 g. potassium ferricyanide and 4 g. of potassium chlorate, in 100 c. c. water, the calculated quantity of hydrochloric acid (4 g., sp. gr. 1.19) in about 75 c. c. water. The solution quickly assumed a peculiar red color, and after a few minutes effervescence was observed, presumably escaping cyanogen chloride. Shortly afterwards the solution was cooled down and allowed to stand for twenty-four hours. Precipitation with alcohol then yielded a crystalline product, which was redissolved in water and reprecipitated with alcohol about twelve times. On the third or fourth repetition of this operation the body began to lose its crystalline nature, and the final product, which he used for his analyses, was completely amorphous. The most characteristic reaction of the new compound, and the only one which indicated that its iron was in the tetravalent state, was found to be its decomposition by alkalies. On being boiled with the latter it yielded ferric hydroxide, potassium ferrocyanide, and potassium cyanate.

The method employed by Skraup is open to criticism at two points. If the reaction proceeds as he supposed, it should be stopped before the evolution of cyanogen chloride begins, for this must be due to the decomposition of the substance. In describing the reactions of the salt, Skraup states that it is slowly decomposed by alcohol. It would hardly seem advisable, therefore, to employ repeated precipitation with alcohol as a means of purifying it. These considerations led us to believe that the final, amorphous body was simply a decompo-

sition-product of the supposedly impure crystalline precipitate obtained on the first addition of alcohol to the oxidized solution, and that this body might perhaps be obtained in a state more suitable for analysis by some other supplementary process.

We therefore prepared this salt according to Skraup's directions, but placed the mixture in ice-water as soon as the first sign of effervescence was observed. The time required for the reaction varies greatly with the temperature. When the hydrochloric acid is added to the boiling solution, the gas comes off at once, but at 95°, the temperature at which we worked, about five minutes are required. When the solution had cooled to almost 20°, it was filtered, and slightly less than an equal volume of alcohol, or just enough to bring about incipient precipitation, was added. The solution was then allowed to stand until its temperature had fallen nearly to 0°. A dense crystalline precipitate separated out, from which the mother-liquid was drawn off as completely as possible, without washing, on a suction filter. The product was then redissolved in as little water as possible, and partially reprecipitated with a much smaller volume of alcohol. On a second repetition of this operation, the crystalline nature of the precipitate became less distinct, as Skraup also observed. The purification was therefore carried no further. The salt was extremely soluble in water, yielding a solution which was green by reflected light, and by transmitted light had a peculiar reddish tint. Thus far it corresponded with Skraup's observations, but on boiling with ammonium hydroxide it gave only a trace of ferric hydroxide and potassium ferrocyanide,* indicating that our supposition was correct, that Skraup's body was a product of decomposition of his first precipitate.

The salt obtained on the third precipitation with alcohol (the yield was about 1 g.) was carefully examined under the miscroscope for impurities. It consisted of very small,

* A quantitative determination of the ferrocyanide thus formed by titration with potassium permanganate, showed that only 0.07 per cent of the salt had undergone reduction.

greenish-yellow needles, among which no foreign ingredients could be seen. The body was, therefore, subjected to analysis, in the expectation that it would give results corresponding closely with the formula $K_2Fe(CN)_6$. To our surprise, however, we found that, together with 11.83 per cent of water, it contained the four elements in the same ratio as potassium ferricyanide itself, corresponding almost exactly with the formula $K_3Fe(CN)_6$. The results of this first analysis (I) follow:

	Calculated for $K_3Fe(CN)_6$ with 11.83 per cent H_2O.	Found.	Ratio.	
H_2O	11.83	11.83	. . .	. . .
Fe	15.01	15.43	0.344	1.03
C	19.30	19.20	1.97	5.91
N	22.51	22.70	2.07	6.21
K	31.35	31.60	1.0	3.0
	100.00	100.76		

The water present we afterwards found to be due chiefly to the extreme difficulty with which the salt can be dried. On precipitation the latter comes down as a network of very fine, delicate needles, in the capillary spaces between which the water is most obstinately retained. By allowing the salt to stand for several days in a vacuum over sulphuric acid, the percentage of water can be reduced until it corresponds with the value calculated for the formula $K_3Fe(CN)_6+H_2O$.* Our first supposition was that the presence of this water was the cause of the difference between the new compound and the normal ferricyanide, or, in other words, that it was water of constitution. This hypothesis, however, is inadmissible; for the corresponding silver salt, which can readily be obtained, is like normal silver ferricyanide, — an anhydrous compound, and has the formula $Ag_3Fe(CN)_6$. The salt must, therefore, be regarded as an actual isomer of potassium ferricyanide. What the structural difference between the two is, or how the isomer happens to be formed through the action of such a substance

* Found, 5.55 per cent. The theory requires 5.18 per cent.

as chloric acid, we cannot explain. But repeated analyses of the compound itself, and also of the silver salt, together with the quantitative study of reactions in which it was completely converted into the normal ferricyanide, leave no doubt as to its composition. Its reactions, on the other hand, are in some cases totally different from those of the latter compound. We propose for it, as a temporary designation, the term potassium β-ferricyanide.

The various analyses of the isomer published below were made from as many different preparations obtained under as varied conditions as possible. In the course of the work it was found that two precipitations with alcohol are sufficient to yield the body in a state pure enough for analysis. Even on the first precipitation it is nearly pure, giving no ferric hydroxide when boiled with ammonia and containing only a trace (about 0.5 per cent) of chlorine. By using somewhat less than an equal volume of alcohol on the second precipitation, a yield of about 15 g. could be obtained, and when the conditions were very carefully observed the individual crystals were large enough to be observed by the naked eye. A slight variation of the conditions in any particular, however, leads to the formation simply of a crystalline paste, which it is almost impossible to purify. The properly prepared salt can be easily and thoroughly washed with 75 per cent alcohol; when placed in a vacuum, after subsequent washing with absolute alcohol, it falls to an extremely light, voluminous powder. This possesses a pure, rich olive color, which appears brown when observed by gaslight. It dissolves with the utmost ease in water, but, unlike Skraup's compound, it is not noticeably hygroscopic. The solution is comparatively stable, though it undergoes gradual decomposition on standing. This decomposition is not accompanied by the formation of either potassium cyanide, hydrocyanic acid, or free cyanogen, nor does the dry salt possess the slightest odor of the latter substance.

Various attempts were made to obtain the salt in the form of larger crystals, by the evaporation of its concentrated

aqueous solution. But owing to the capillary action of the needles as they separated on the sides of the vessel, only a dense efflorescent growth was obtained, from which no individual crystals could be isolated. Analysis II below is from one of these crops. When a small quantity of the salt is dissolved in a drop or two of water and allowed to crystallize out on an object glass, it is obtained as an intimate network of microscopic needles, of characteristic, very slightly tapering form. They are probably rhombic, showing parallel extinction and slightly pleochroic. Among them no trace of the heavy prismatic or block-shaped crystals of the normal or *a*-ferricyanide could be detected. In crsytallization experiments with mixtures of the two isomers, on the other hand, they could be distinguished at a glance, showing that the new compound is not merely the *a*-ferricyanide in a new crystallographic modification.

Analytical Results. — For the determination of potassium and iron the compound was decomposed by heating with concentrated nitric acid. The iron was then precipitated with ammonium hydroxide, and the potassium weighed as chloride or sulphate. The nitrogen was determined by combustion. The total combustion of the carbon takes place with great difficulty, and the results for that element were rather low (one per cent or more). In view of the above determination, (I) however, together with experiments on the quantitative conversion of the compound into potassium *a*-ferricyanide, its further determination was deemed unnecessary, and the percentage of cyanogen was calculated from that of the nitrogen. The water was determined by combustion.

	II.		III.	
	Found. Per cent.	Ratio.	Found. Per cent.	Ratio.
CN . .	45.31	6.00	45.13	6.15
Fe . . .	16.95	1.04	16.02	1.01
K . . .	33.91	3.00	32.90	3.00
H_2O . .	5.41	1.00	4.65	0.8
	101.47		98.70	

IV.

	Found.	Ratio.	Average of the 3 Analyses.	Calculated for $K_3Fe(CN)_6.H_2O$.
CN . .	45.05	5.94	45.16	44.96
Fe . .	16.98	1.05	16.65	16.14
K . . .	34.11	3.00	33.64	33.72
H_2O . .	4.73	0.87	4.93	5.18
	100.87		100.38	100.00

A subsequent determination of water, according to the method of Jannasch and Locke,* in another preparation which had previously been allowed to stand in a vacuum over sulphuric acid for three days, gave 5.55 per cent. There seems to be no doubt, therefore, that the body possesses the formula $K_3Fe(CN)_6.H_2O$. In order to prove this definitely, however, and at the same time make a direct estimation of the cyanogen, a method was sought by which the body could be quantitatively converted to the *a*-ferricyanide. Preliminary experiments showed that it passed into potassium ferrocyanide upon reduction, but its titration on that principle, either according to the method of Mohr † or after reduction with ferrous hydroxide, gave no satisfactory results. The most convenient means of reduction we found to be sodium amalgam in alkaline solution. This converted the substance completely into the ferrocyanide, without the separation even of traces of iron. The ferrocyanide was then titrated with potassium permanganate in sulphuric acid solution. The details of the method were first worked out with potassium *a*-ferricyanide, and the best conditions found to be as follows: The solution of the salt (about 0.2 g.) in 100 c. c. of water, was rendered slightly alkaline with sodium carbonate, and a piece of 5 per cent sodium amalgam was then added. During the reduction the solution was kept on the steam-bath. In the course of an hour or so the mercury was filtered off and the solution cooled and very slightly acidified with sulphuric acid. It was then titrated with a solution of permanganate until the red color of the latter remained for half a minute or more.

* Zeitschr. anorg. Chem., vi, 174. † Ann. Chem. (Liebig), cv, 62.

With potassium *a*-ferricyanide the following results were obtained:

1 c. c. $KMnO_4$ solution = 0.00572 g. Fe = 0.0336 g. $K_3Fe(CN)_6$.

	$K_3Fe(CN)_6$ taken.	C. c. $KMnO_4$ solution used.	C. c. $KMnO_4$ calculated.
	g.		
I . . .	0.2596	7.65	7.72
II . . .	0.2402	7.10	7.15
III . . .	0.1926	5.70	5.71

The same method of procedure gave for the new compound the following results:

	$K_3Fe(CN)_6.H_2O$ taken.	C. c. $KMnO_4$ solution used.	C. c. $KMnO_4$ solution calculated.
	g.		
I . . .	0.1611	4.55	4.55
II . . .	0.2520	7.20	7.11
III . . .	0.1946	5.40	5.49
IV . . .	0.2641	7.35	7.45
V . . .	0.1427	4.10	4.04
VI . . .	0.2208	6.30	6.26

In order to make sure that in these experiments only potassium *a*-ferricyanide remained in the solutions, or, in other words, that the conversion of the *β*-ferricyanide to the latter compound was absolutely quantitative, the amount of *a*-ferricyanide which the solutions in V or VI contained was gravimetrically determined. This was accomplished by precipitating the titrated solutions with silver nitrate, and estimating the percentage from the silver, which was weighed as chloride. The results were very exact, the amount of silver found differing by little more than a milligram from that required by theory:

V Found, 0.1347 g. Ag = 0.1367 g. $K_3Fe(CN)_6$.
Calculated, 0.1332 g. Ag = 0.1352 g. $K_3Fe(CN)_6$.
VI Found, 0.2048 g. Ag = 0.2079 g. $K_3Fe(CN)_6$.
Calculated, 0.2061 g. Ag = 0.2092 g. $K_3Fe(CN)_6$.

The average percentage of cyanogen in the *β*-ferricyanide,

as calculated from these six determinations, is 45.07. The theory requires 44.96 per cent.

Potassium β-ferricyanide, like the normal salt, yields characteristic precipitates with the solutions of most of the heavy metals. These have, in general, the same characteristics as the corresponding α-ferricyanides, and in some cases *pass over into the latter with extreme ease.* The less notable of these precipitates are collected briefly in the table below, in which, for the sake of comparison, the α-ferricyanides are also included. The reactions examined were brought about in 2 per cent solutions. In the case of silver, bismuth, stannic tin, and lead, the reactions will be discussed more fully, as they present characteristic points of difference between the two ferricyanic groups.

	β-Ferricyanides.	α-Ferricyanides.
Cd.	Dirty green, soluble in $(NH_4)_2CO_3$,HCl, insoluble in HNO_3.	Pale yellow, soluble in $(NH_4)_2CO_3$,HCl, insoluble in HNO_3.
Cu.	Yellowish-green, insoluble in HNO_3 or HCl.	Dark greenish-yellow, insoluble in HNO_3 or HCl.
Fe^{III}.	Dark yellow coloration, blue precipitate on boiling.	Dark red coloration, blue precipitate on boiling.
Fe^{II}.	Blue precipitate.	Blue precipitate.
Hg^{II}.	No precipitate.	No precipitate.
Co.	Dark red precipitate, insoluble in HCl or HNO_3.	The same.
Mn.	Brown precipitate, insoluble in NH_4OH, HCl, or HNO_3.	The same.
Hg^{I}.	Yellowish-green, flocculent precipitate. Rapidly undergoes reduction on boiling, becoming blue.	Pale yellow, undergoes reduction only slowly on boiling.
Ni.	Dark yellowish-green, insoluble in HNO_3 or HCl.	Light yellow, same behavior.
Zn.	Yellowish-green, soluble in HCl, $(NH_4)_2CO_3$, insoluble in HNO_3.	Yellow, same behavior.

The *β*-ferricyanides of these metals, as is seen, resemble the *a*-compounds in nearly all particulars, being distinguished from them chiefly in having a more or less pronounced green color. It might be supposed, therefore, that they are identical with them, but colored by slight impurities. But the behavior of the salts of bismuth, stannic tin, lead, and silver shows that this is not the case. Bismuth *a*-ferricyanide is a very sparingly soluble, straw-colored precipitate, which is deposited even from very dilute solutions of potassium ferricyanide on addition of bismuth nitrate. It is likewise insoluble in concentrated nitric acid. *A solution of potassium β-ferricyanide, on the other hand, when freshly prepared, gives no trace of a precipitate with bismuth nitrate.* The solution assumes a slightly greenish tint, but even when concentrated remains otherwise unaltered for some time. On standing, and especially when exposed to the action of the direct sunlight, it deposits large granules of a black, crystalline compound, which we have not yet fully examined, but which is apparently bismuth ferrocyanide.

Stannic chloride, on the other hand, yields no precipitate with potassium *a*-ferricyanide, but precipitates the isomer completely. The resulting compound comes down as a slimy, pure green body, which is insoluble in either hydrochloric or nitric acid. We have, however, been unable to obtain it in a state suitable for analysis.

A comparative study of the lead salts was kindly undertaken by Mr. H. A. North. While lead ferricyanide is not precipitated by potassium *a*-ferricyanide, under ordinary circumstances, it is much less soluble in water than either the latter compound or lead nitrate. When concentrated solutions of the two are mixed in the proper proportions, it slowly separates out in large, dark-red crystals.* Mr. North made this salt by dissolving the calculated quantities, or 3 g. each, of potassium ferricyanide and lead nitrate in 7 c. c. and 8 c. c. of water, respectively. On allowing the mixed solutions to stand for a few minutes, he obtained more than a gram of

* Rammelsberg, J. prakt. Chem. (2), xxxix, 455.

well-crystallized lead ferricyanide. A similar experiment was then made, with exactly the same quantities, potassium β-ferricyanide being used instead of the α-salt. No crystallization took place, indicating that lead β-ferricyanide is much more soluble in water than its isomer. This solution was allowed to stand over night, and by morning, in addition to an efflorescent product, more or less of the normal lead α-ferricyanide had crystallized out, the β-ferricyanide having partially passed over into the latter compound. The solution then gave the usual straw-colored precipitate with bismuth nitrate, with which it had not reacted twelve hours before.

Various attempts were made to isolate the β-lead salt by other means, but without much success. The most satisfactory results were obtained by dissolving lead oxide in glacial acetic acid, and adding to the solution the calculated quantity of potassium β-ferricyanide, dissolved in 25 c. c. of glacial acetic acid and 7 c. c. of water. A green, amorphous precipitate separated out, which was readily soluble in water forming a greenish-red solution, and this yielded no precipitate with bismuth nitrate. An analysis of the product showed that it contained 49 per cent lead, and no potassium, but no simple atomic ratio was evident between the lead and nitrogen, which was somewhat low. It is probable, therefore, that the body was a mixture. An experiment made with potassium α-ferricyanide, in a similar manner, yielded a crystalline precipitate of the ordinary lead ferricyanide.

The most interesting β-ferricyanide of a heavy metal which we have obtained is the silver salt. This is thrown down quantitatively as a dark brown, flocculent precipitate, which can be readily filtered and washed.* Its most marked characteristic is the ease with which it passes into the α-ferricyanide. This takes place simply when the precipitate, suspended in its mother-liquid, is heated to 100°. The conversion is indicated by the change in color to the bright orange of the α-ferricyanide. The silver salt was prepared for analysis by adding the potassium salt to a slight excess of silver nitrate, both being in

* On drying it forms a light, brown powder.

ice-cold solution. The precipitate was washed with ice-water, then with alcohol, and finally with ether, to secure rapid drying, and then allowed to stand in a vacuum, without exposure to light. The results of the analyses were as follows:

	Calculated for $Ag_3Fe(CN)_6$.	Found. I.	Found. II.
Ag	60.47	59.41	60.00
Fe	10.45	10.84	. . .
N	15.67	15.31	. . .

The readiness with which the silver salt passes into silver *a*-ferricyanide presented another means of ascertaining whether the conversion of the one ferricyanic group into the other is actually quantitative. Weighed quantities of the potassium salt were precipitated with silver nitrate in the cold, and one of the precipitates (I) then rapidly heated in its mother-liquid until it had assumed the orange-red color of silver *a*-ferricyanide. The silver in each of the precipitates was then determined, and found to be as calculated for the compound $Ag_3Fe(CN)_6$.

I 0.2912 g. $K_3Fe(CN)_6.H_2O$ gave 0.2729 g. Ag.
calculated 0.2724 g. Ag.
II 0.2470 g. " " gave 0.2291 g. Ag.
calculated 0.2307 g. Ag.

The filtrates were then very thoroughly examined for products other than potassium nitrate. The filtrate from (I) contained a trace of iron, which was precipitated and weighed. It amounted only to 0.15 per cent of the potassium salt. In neither filtrate could either hydrocyanic or cyanic acid be detected. The change which the silver salt undergoes on heating must therefore be assumed to take place without the formation of any substance other than silver *a*-ferricyanide, and to consist simply in a rearrangement of atoms in the molecule $Ag_3Fe(CN)_6$.

It was hoped that by acting on the silver salt with the calculated quantity of hydrochloric acid the free *β*-ferricyanic acid could be prepared. The solution obtained gave for the

moment no precipitate with bismuth nitrate, showing that the β-acid had been formed, but the latter passed within a few minutes into the normal acid, and then into further decomposition-products. Efforts to prepare the salts of calcium and barium in the same way also failed, the normal ferricyanides being finally obtained.

In regard to the constitution of the β-ferricyanic group we have little to state. Any attempt to assign a definite structural formula to it would, for the present, be pure speculation. The suggestion offers itself that one of the two isomers contains isonitril groups, the other nitril groups. But this view, at least, is absolutely refuted by the identical behavior of the two on reduction. So far as we can find, there are no cases known where isomers containing respectively the —CN and —NC groups yield the same product with nascent hydrogen. On the other hand, if both ferricyanides contain only cyanogen groups, the β-compound becomes of especial importance because of its bearing on Werner's theory. According to the latter the ferricyanic group is not to be represented by the structural formula, but simply as a radical in which the cyanogen groups occupy "co-ordination positions" about the ferric atom. Isomerism between two equivalent $Fe(CN)_6$ groups, if this is so, can be due only to stereochemical causes. The greatest value of Werner's theory lies in the explanation which it offers of the cases of isomerism among the platinamine and cobaltiamine compounds. The six co-ordinated groups are supposed to occupy the angles of a regular octahedron, in the centre of which is the metal. Isomerism is then possible whenever two or more of the co-ordinated groups differ from the others. But according to it a radical in which they are all alike, such as $Fe^{III}(CN)_6$, cannot have two different configurations, or, in other words, exist in isomeric modifications. It would seem, therefore, that the existence of potassium β-ferricyanide stands in direct contradiction to such a theory, at least in its present form.

It may of course be that the β-ferricyanide is a mixture of two substances in proportions giving the atomic ratio

$K_3Fe(CN)_6$. But throughout all our investigations we have searched for, and failed to find, a single indication that such is the fact. Its completely crystalline and homogeneous appearance, the constant composition of different products, and all its observed reactions point closely to its being an individual chemical compound. Our investigations will be continued, however, and we hope to bring more light to bear upon the subject within a short time.

NEW HAVEN, December 12, 1898.

ON THE FORMATION OF POTASSIUM β-FERRICYANIDE THROUGH THE ACTION OF ACIDS UPON THE NORMAL FERRICYANIDE.*

By JAMES LOCKE and GASTON H. EDWARDS.

We have shown in a previous paper† that when a solution of potassium ferricyanide is heated for a short time with potassium chlorate and hydrochloric acid, an isomer of this salt is obtained, which crystallizes with one molecule of water. This salt had already been obtained by Skraup‡ and others, in an impure state, by the action of oxidizing agents, and was regarded by them as an oxidation product of the normal ferricyanide, with the formula $K_2Fe(CN)_6$. At the time of our first investigation we likewise ascribed its formation to the oxidizing action of the potassium chlorate, but have since found that it is due to the hydrochloric acid alone, and is, in fact, formed more or less readily by the action of any acid on potassium ferricyanide. Its preparation by former experimenters can thus be readily explained, as their operations were all carried on in acid solutions.

In our first experiments to investigate this point we used the same quantity of hydrochloric acid as in the preparation of the salt with potassium chlorate, that is, the amount required according to the equation given by Skraup,

$$6K_3Fe(CN)_6 + KClO_3 + 6HCl = 6K_2Fe(CN)_6 + 7KCl + 3H_2O,$$

and otherwise performed the experiments exactly as described in our previous article. 50 g. of potassium ferricyanide were dissolved in 100 c. c. of water, heated to boiling, and 18 c. c. of concentrated hydrochloric acid (sp. gr. 1.19), diluted

* Amer. Chem. Jour., xxi, May, 1895.

† Ibid., 193.

‡ Ann. Chem. (Liebig), clxxxix, 368.



FIG. I.—Potassium β-ferricyanide.

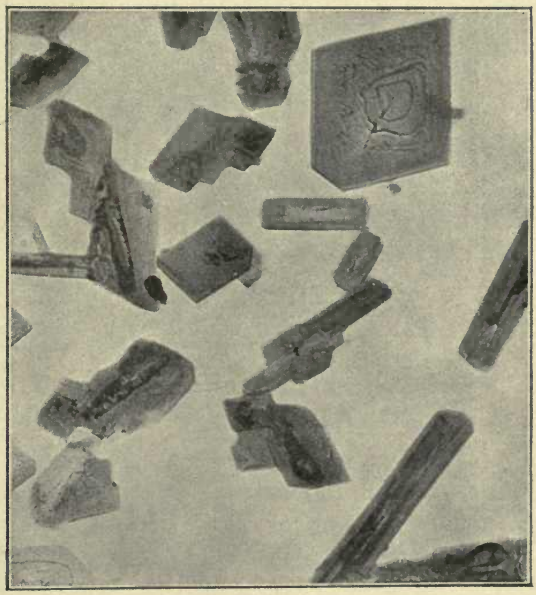


FIG. II.—Potassium α-ferricyanide.

with three times their volume of water, were added, and the mixture allowed to stand on the water-bath. Small portions were taken out at short intervals, cooled, precipitated with equal volumes of 95 per cent alcohol, and the precipitates filtered off. These various preparations were then tested with bismuth nitrate, with which the *α*-ferricyanide gives a yellow precipitate, and the *β*-ferricyanide none. Subsequently the percentages of cyanogen which they contained were determined by reduction with sodium amalgam, and titration to potassium *α*-ferricyanide with potassium permanganate.*

Two samples of the solution, taken out after the reaction had proceeded one and one-half minutes and three minutes, respectively, gave with alcohol yellow and yellowish-green precipitates, the colors of which were due to the presence of unchanged *α*-ferricyanide. These showed, with bismuth nitrate, the test characteristic of the latter. At the end of five minutes the originally reddish-yellow solution had assumed the peculiar red-violet color of the *β*-salt, and the precipitated samples then consisted of a completely homogeneous mass of well-formed, olive-green crystals. These showed all the properties of potassium *β*-ferricyanide, $K_3Fe(CN)_6.H_2O$, as previously described by us. They are most readily recognized by their very characteristic crystal-habit, showing the forms illustrated in Fig. 1. This is taken from a photomicrograph, as is also Fig. 2, which shows crystals of the normal ferricyanide obtained under similar conditions. At the same time the percentage of cyanogen rapidly fell to a value corresponding closely to that calculated for the *β*-salt; that is, 44.96 per cent. The sample obtained after the reaction had proceeded for ten minutes was of a greenish-black color, and showed no distinct crystallization, indicating that further decomposition had taken place. In this, and subsequent samples also, the percentage of cyanogen had fallen considerably below the value for the *β*-compound.

The analytical results of this series of experiments are tabulated below:

* Amer. Chem. Jour., xxi, 193.

Series A.

50 g. $K_3Fe(CN)_6$; 18 c. c. conc. HCl.
1 c. c. $KMnO_4$ solution = 0.03704 g. $K_3Fe(CN)_6$.

No.	Time. Min.	Color.	Weight of substance taken. g.	C. c. $KMnO_4$ used.	C. c. $KMnO_4$ calculated for $K_3Fe(CN)_6.H_2O$.	C. c. $KMnO_4$ calculated for $K_3Fe(CN)_6$.	Cyanogen found.
I	1½	yellow	0.1881	4.9	4.81	5.08	45.74
II	3	yellowish-green	0.2616	6.8	6.70	7.06	45.65
III	5	olive	0.2073	5.3	5.31	5.59	44.89
IV	7½	olive	0.2919	7.4	7.47	7.88	44.52
V	10	green-black	0.2376	5.9	6.08	6.42	43.60
VI	15	green-black	. . .	. .	. . .	. . .	. . .
VII	20	green-black	0.3014	7.3	7.71	8.17	42.53

Cyanogen calculated for $K_3Fe(CN)_6$, 47.41 per cent.
" " " $K_3Fe(CN)_6.H_2O$, 44.96 per cent.

The question next suggested itself, whether it was necessary to have hydrochloric acid present in definite molecular quantity, as above, or whether its action was not merely one of catalysis, and caused by the presence even of small quantities. In order to decide this, experiments similar to the above were made, in which one-half, one-fourth, and one-eighth of the amount of the acid there used was employed. It was found, not only that the β-compound was formed in each case, but that its subsequent decomposition by the acid takes place much more slowly than when the acid is more concentrated. The reactions could, therefore, be much more easily followed in these experiments, as a considerable interval elapsed between the point at which the α-salt disappeared and that at which the β-salt noticeably began to decompose. The results of these experiments are tabulated below:

Series B.

50 g. $K_3Fe(CN)_6$; 9 c. c. conc. HCl.

No.	Time. Min.	Color.	Weight of substance taken. g.	C. c. $KMnO_4$ used.	C. c. $KMnO_4$ calculated for $K_3Fe(CN)_6 \cdot H_2O$.	C. c. $KMnO_4$ calculated for $K_3Fe(CN)_6$.	Cyanogen found.
I	5	yellowish-green	0.2152	5.6	5.51	5.81	45.74
II	10	olive	0.2222	5.7	5.68	5.90	45.03
III	15	olive	0.2233	5.7	5.72	6.03	44.82
IV	20	green-black	0.2155	5.2	5.52	5.82	42.37
V	25	green-black	0.2393	5.7	6.12	6.49	41.83

Series C.

50 g. $K_3Fe(CN)_6$; 4.5 c. c. conc. HCl.

I	2	yellow	0.3535	9.3	9.05	9.54	46.19
II	4	yellowish-green	0.3421	8.9	8.75	9.24	45.68
III	6	olive	0.1901	4.9	4.86	5.13	45.26
IV	8	olive	0.2569	6.6	6.57	6.94	45.11
V	10	olive	0.2263	5.8	5.79	6.11	45.00
VI	15	olive	0.2223	5.7	5.69	5.90	45.03
VII	20	green	0.1994	5.0	5.10	5.38	44.03
VIII	25	green-black	0.3195	8.0	8.18	8.63	44.00
IX	30	green-black	0.2198	5.5	5.63	5.93	43.94

In Series *D* it will be seen that in the first fifteen minutes the percentage of cyanogen fell from the value calculated for the *α*-salt, or 47.41 per cent, to 45.02 per cent, or nearly the value calculated for the *β*-salt, a loss of 2.4 per cent. From this point on, the precipitated samples gave no reactions with bismuth nitrate. During the next twenty minutes the percentage of cyanogen fell only 0.45 per cent, and the fractions taken out in this interval were all thoroughly homogeneous and well crystallized. Beyond this point the decomposition again became more rapid, and the samples obtained were of far less satisfactory appearance than those in numbers III–VI.

Series D.

50 g. $K_3Fe(CN)_6$; 2.25 c. c. conc. HCl.

No.	Time. Min.	Color.	Weight of substance taken. g.	C. c. $KMnO_4$ used.	C. c. $KMnO_4$ calculated for $K_3Fe(CN)_6.H_2O$.	C. c. $KMnO_4$ calculated for $K_3Fe(CN)_6$.	Cyanogen found.
I	5	yellow	. . .	. .	. . .	. . .	. . .
II	10	yellow	0.2256	5.9	5.77	6.06	45.92
III	15	yellowish-green	0.1510	3.9	3.86	4.08	45.02
IV	20	olive	0.2121	5.4	5.43	5.73	44.71
V	25	olive	0.2584	6.6	6.61	6.98	44.85
VI	35	olive	0.2639	6.7	6.75	7.12	44.57
VII	45	olive	0.2113	5.3	5.41	5.70	44.04
VIII	55	green	0.2036	5.0	5.21	5.50	43.12
IX	65	green-black	0.2171	5.4	5.55	5.86	43.67
	Hours.						
X	1½	green-black	0.1745	4.2	4.46	4.71	42.27
XI	2	green-black	0.2015	4.9	5.17	5.42	42.70
XII	2½	green-black	0.2010	4.5	5.14	5.43	39.31

In Series *B* and *C* similar results were obtained, but the reactions proceeded much more rapidly. In *C*, for instance, the samples ceased to react with bismuth nitrate in eight minutes, and the β-salt was noticeably decomposed at the end of twenty minutes. It must, therefore, be concluded that the velocity of the reaction is directly dependent upon the concentration of the acid.

Similar results were obtained when other acids were substituted for hydrochloric acid. Experiments were instituted with sulphuric, oxalic, and acetic acids. No quantitative determinations were made, however, as it was found impossible, in the first two cases, to obtain the precipitates free from potassium sulphate and potassium oxalate. But that the reaction proceeded in the same way as when hydrochloric acid was used, was readily recognized by the color of the solution and by the appearance of the precipitates. With oxalic acid the β-salt was formed less readily than with sulphuric acid,

though in both cases the conversion of the *α*-salt into its isomer took place more slowly than it did in hydrochloric acid solution. It would thus appear that the catalytic action of different acids, to which the formation of the *β*-salt is due, is directly dependent upon the degree to which the acid used undergoes ionization. According to this, an acid such as acetic, which ionizes but slightly, should have only a very slow action. This was found to be the case, for with dilute acetic acid we could obtain no *β*-salt at all, and a solution of ferricyanide, heated for an hour with the concentrated acid (2 molecules), still gave a slight precipitate with bismuth nitrate.

NEW HAVEN, February, 1899.

ON THE SEPARATION OF TUNGSTIC AND SILICIC ACIDS.

By H. L. WELLS and F. J. METZGER.

In a recent number of a German periodical* appears an article by Otto Herting of Philadelphia in which the assertion is made that the method given in the text-books for expelling silica from tungstic acid by means of hydrofluoric acid is incorrect. This statement is made on the ground of alleged numerous quantitative experiments with mixtures of pure tungstic acid and pure ignited silicic acid, but no details in regard to the results are given. Herting believes that upon ignition silicic and tungstic acids form a silico-tungstic acid which is volatile when treated with hydrofluoric acid, and finally says that he should be pleased if by means of his article he should bring about the more careful study of the "action of hydrofluoric acid upon tungstic acid in the presence of silicic acid."

Since Herting's statement throws doubt upon a method that is generally used, we have undertaken an examination of the matter. For this purpose we dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly with sulphuric acid of sp. gr. 1.378 to separate any molybdic acid that might possibly be present,† washed the residue and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible was mixed with about an equal quantity of pure silica. The mixture was covered with dilute sulphuric acid, a liberal amount of pure hydrofluoric acid was added, the liquid was carefully evaporated and the residue was ignited over a *Bun-*

* Zeitschr. f. angew. Chem., 1901, 165.

† See Ruegenberger and Smith, Jour. Amer. Chem. Soc., xxii, 772.

sen burner. Then another portion of silica was added and the operation was repeated. The results are shown in the following table:

	Taken.		WO_3 found after	
	WO_3	SiO_2	1st operation.	2d operation.
	g.	g.	g.	g.
I	.1928	.2	.1927	.1928
II	.2097	.2	.2097	.2096
III	.2100	.2	.2099	.2100
IV	.1999	.2	.2000	.1998

The greatest error found in these experiments is .0001 g., and they show that the process is perfectly exact under these conditions.

Other experiments showed that long ignition of the mixed tungstic and silicic acids over the Bunsen burner before expelling the silicic acid had absolutely no effect upon the results.

It was thought that in the absence of sulphuric acid a loss might occur by the treatment of tungstic acid with hydrofluoric acid, and the following experiments were made to test this point, no sulphuric acid being used: —

Taken.		Found.
WO_3	SiO_2	WO_3
g.	g.	g.
.1983	.2	.1983
.2102	.2	.2100
.2106	.2	.2105
.1996	.2	.1994

In these experiments the greatest error, .0002 g., is well within reasonable limits; hence it is evident that the absence of sulphuric acid has no effect. It is to be noticed that in these cases also the tungstic acid was ignited by the *Bunsen flame* only.

Attention should be called to the fact that tungstic acid must not be ignited by means of the blast-lamp, since at the temperature thus produced it volatilizes to a considerable extent. The books of reference do not give proper warning in regard to this matter. The following table gives the results of a series of experiments made by heating over the blast-lamp

in a platinum crucible some of the substance, which showed no loss of weight over the Bunsen burner.

	Weight of WO_3. g.	Loss. g.
Taken	.3007	. . .
Ignited for 2 minutes	.2978	.0029
" " " again . . .	.2962	.0016
" " " " . . .	.2946	.0016
" " " " . . .	.2932	.0014
" " " " . . .	.2924	.0008
" " " " . . .	.2916	.0008
" " " " . . .	.2906	.0010
" 5 " " . . .	.2872	.0034
Total loss,		.0135

All the ignitions except the last were made with a lamp provided with a water-blast, which gave a flame of only moderate power. The last ignition was made with a lamp connected with a foot-bellows, which gave a considerably higher temperature. It is noticeable that the losses show a tendency to diminish after the first ignition, but this is probably due to a change in the physical condition of the oxide rather than to the removal of some more volatile substance. It is hardly possible that our carefully purified tungstic acid, which showed no loss when heated with a good Bunsen burner, could contain an amount of molybdic acid or other volatile substance sufficient to give the results that have been obtained. The loss shown in the table above amounts to nearly 5 per cent, while in another experiment .1955 g. of tungstic acid lost over 7 per cent after heating with the blast-lamp for twenty minutes. It should be stated that the platinum crucible in which these ignitions were made showed no loss in weight after it had been cleaned.

We have shown that Herting's criticism of the usual method for separating silicic and tungstic acids is without foundation, and it appears probable that his difficulties were due to igniting tungstic acid at a too elevated temperature.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

ON A SALT OF QUADRIVALENT ANTIMONY.

By H. L. WELLS and F. J. METZGER.

While engaged in purifying some cæsium material, we precipitated a large quantity of the salt $Cs_3Sb_2Cl_9$ by adding an excess of antimony trichloride to a hydrochloric acid solution of impure cæsium chloride. A small amount of cæsium remained in the filtrate, and, wishing to recover this, we added some lead nitrate solution, and passed chlorine gas into the liquid in order to precipitate the very insoluble lead tetrachloride salt, Cs_2PbCl_6.* Much to our surprise, the precipitate, while showing the usual octohedral form, was bright green in color, whereas the pure lead salt is bright yellow. The product was found to contain a small quantity of antimony, and by preparing the lead salt after the addition of varying quantities of antimony trichloride we obtained products of various colors, from yellowish green to dark bluish green. The following determinations were made in a lighter and a darker product:

	Light green.	Dark green.
Antimony . . .	0.92 per cent	1.44 per cent

These results indicated that antimony was not an essential constituent of the compound, and it seemed probable that some salt of antimony isomorphous with Cs_2PbCl_6 had crystallized with it. We drew the further inference that the isomorphous antimony compound must be strongly colored, probably blue. Fortunately we had access to the reprint of an article by Setterberg † (which, as far as we can find, has not been noticed in any of the books of reference) where a peculiar black cæsium-antimony salt is described. Setterberg

* Amer. Jour. Sci. (3), xlvi, 180.

† Öfversigt K. Vetensk.-Akad. Förhandl., 1882, 23.

made this compound by boiling a solution of antimony trichloride in strong hydrochloric acid with antimony pentachloride and cæsium chloride in excess. He ascribes to it the formula $2CsCl.SbCl_4$ or $4CsCl.SbCl_3.SbCl_5$, and states that it forms black, very small, short prisms. It was evident that a salt of this composition might be expected to crystallize with $2CsCl.PbCl_4$, and if so, the fact would be a strong argument in favor of Setterberg's first formula, but his description of the form of the salt gave no evidence of the isomorphism of the two compounds.

We have prepared Setterberg's salt under varying conditions, and have confirmed his formula, as is shown by the following analysis of a very pure product:

	Found.	Calculated for Cs_2SbCl_6.
Cæsium	44.92	44.41
Antimony	20.23	20.03
Chlorine	35.13	35.56
	100.28	100.00

As far as can be judged by careful microscopic examination, this salt crystallizes in perfect octahedra. We could find no indication of a prismatic form corresponding to Setterberg's description; hence it is probable that his crystals were so small that he did not make them out clearly. No optical examination of the crystals could be made on account of their complete opacity. The color of the crystallized substance is absolutely black, but when a little of it is rubbed between the ground surfaces of a glass-stoppered bottle, it shows a very strong, dark blue color.

From the crystalline form and color of this curious salt there can be no doubt that it was the substance which gave the green color to our products of Cs_2PbCl_6, and it seems certain that the two salts are isomorphous. The color of the antimony salt indicates that it is not a compound containing antimony trichloride and pentachloride, for the known cæsium double salts with these chlorides, $3CsCl.2SbCl_3$ and

$CsCl.SbCl_5$,* are colorless or nearly so, We are convinced, therefore, that this black salt, Cs_2SbCl_6, is a member of the well-known group of octahedral double halides of quadrivalent elements, among which are K_2PtCl_6, Cs_2SrCl_6, Cs_2TeCl_6, Cs_2TeI_6, K_2PbCl_6, and Cs_2PbCl_6, and that it is a double salt of antimony tetrachloride, $SbCl_4$.

Judging from the color of the double salt, the tetrachloride $SbCl_4$ must be black. This color would be entirely unexpected, since $SbCl_3$ and $SbCl_5$ are colorless. We have tried in vain to get some evidence of the separate existence of a black chloride by making mixtures of the two known chlorides at low and high temperatures and by treating the salt Cs_2SbCl_6 with cold concentrated sulphuric acid.

The oxide of antimony Sb_2O_4, or SbO_2, is usually regarded as a compound of Sb_2O_3 and Sb_2O_5. It is possible that this may be a true dioxide, but it would be expected that an oxide which corresponded to a black chloride would be black also, for, if there is a difference in color, oxides are usually darker than the corresponding chlorides.

We have prepared a jet-black double bromide by using a method exactly similar to that by means of which the black double chloride was made. Judging from analogy, this is probably Cs_2SbBr_6, but we were unable to get a product that was pure enough for analysis, as it was always mixed with more or less light-colored impurity. We attempted, without success, to make the corresponding iodide and fluoride.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

* Setterberg, loc. cit.

ON THE PURIFICATION OF CÆSIUM MATERIAL.

By H. L. WELLS.

SEVERAL years ago* I recommended the use of the yellow salt $2CsCl.PbCl_4$ as a means of precipitating cæsium from its solutions. Subsequent experience has shown that the method is very convenient for removing small quantities of the rare metal from all sorts of solutions, particularly from those from which the greater part of it has been precipitated by other means. For large quantities of cæsium, however, the lead tetrachloride method, used alone, is inconvenient on account of the large amount of chlorine that must be used, and because it is possible to obtain only very dilute solutions of lead chloride or of the white double salt $CsCl.2PbCl_2$.†

I have used extensively the salt just mentioned, as a means of precipitating cæsium from concentrated solutions of the crude extract of pollucite made by means of hydrochloric acid. The precipitation is made by adding a hot, concentrated solution of the calculated amount of lead nitrate. The precipitate is crystalline and can be readily washed with dilute hydrochloric acid, then it can be very easily decomposed by boiling with ammonium carbonate solution. The method is satisfactory in a case where very little potassium and practically no rubidium are present, for although it does not give a good separation from these metals, the precipitation of cæsium is nearly complete. The precipitate $CsCl.2PbCl_2$, however, is very heavy compared with the amount of cæsium that it contains, and its decomposition with ammonium carbonate produces four molecules of ammonium chloride for one of cæsium chloride. For these reasons the method has been abandoned in this laboratory in favor of the method of Godeffroy.

* Amer. Jour. Sci. (3), xlvi, 186. † Ibid. (3), xlv, 121.

In precipitating cæsium according to Godeffroy's method I am accustomed to use less concentrated hydrochloric acid solutions than those that have been recommended. About one-third or one-half of the total volume of concentrated hydrochloric acid answers very well, and a solution of this kind possesses the advantage that it can be filtered by means of paper. To such a solution antimony trichloride, also dissolved in hydrochloric acid, is added as long as a precipitate forms. The latter is collected, best on a Büchner filter, and well washed with cold dilute hydrochloric acid.

To the filtrate and washings from the antimony salt, without concentrating them, lead nitrate is added at the rate of 2 or 3 g. per liter. This salt should be dissolved in water before it is added. Chlorine gas is then passed in until the solution is saturated with it. After standing for a few hours the liquid is decanted from the precipitate of Cs_2PbCl_6 (which is usually colored green from the presence in it of the dark blue salt Cs_2SbCl_6*) and is tested by the addition of a little more lead nitrate, and chlorine also if necessary. This precipitation is so complete, as far as cæsium is concerned, that the liquid may be finally discarded. A liter of such a liquid will probably hold in solution only about 0.1 g. of Cs_2PbCl_6, but the rubidium salt is nearly 100 times more soluble. The lead tetrachloride salt should be washed on a Büchner funnel with cold, dilute hydrochloric acid.

Formerly I was accustomed to decompose the antimony salt $3CsCl.2SbCl_3$† by suspending it in water and passing in hydrogen sulphide gas, but for large quantities this is a very slow and laborious operation, and it is much more convenient to treat it in a large porcelain dish with boiling dilute ammonium hydroxide. The antimonious oxide thus produced is dense and easy to filter and wash; moreover it

* Concerning this compound, see the preceding article.

† The composition of this compound was very incorrectly determined by Godeffroy, who gave it the formula $6CsCl.SbCl_3$. Setterberg first arrived at the correct formula, which was afterwards confirmed by Remsen and Saunders, and also by Muthmann, and by Wells and Foote.

may be readily dissolved in hydrochloric acid and used again for precipitating cæsium. A little antimony goes into solution in the ammonia, but this is readily removed, best after the liquid has become slightly acid by evaporation, by passing in hydrogen sulphide and filtering.

The removal of ammonium chloride on a large scale by ignition is a very slow operation. It is therefore best, in most cases, after the hydrogen sulphide has been removed by evaporation, to add to the concentrated solution of cæsium and ammonium chlorides, in a large porcelain dish, a liberal amount of concentrated nitric acid and to heat cautiously until frothing has ceased. When further additions of strong nitric acid produce no change of color or evolution of gas upon heating, the ammonium salts are entirely destroyed and the cæsium chloride changed to nitrate.* The solution of cæsium nitrate in nitric acid is then evaporated to dryness, and the residue is heated until the acid nitrate † is decomposed, and the normal nitrate is more or less completely fused. The evaporation to dryness of the nitrate in the presence of nitric acid over a free flame in a dish is not a difficult operation, since decrepitation takes place to a much less extent than is the case when the chloride is evaporated in the same way. A large mass of fused cæsium nitrate should not be allowed to solidify quietly in the bottom of a porcelain dish, for on cooling it is liable to break the dish by its contraction. If it is stirred as it solidifies, this danger is avoided.

Cæsium nitrate is one of the most beautiful of salts for recrystallization. Like potassium nitrate, it is much more soluble in hot water than in cold, and it crystallizes upon slowly cooling a hot concentrated solution in the form of large colorless prisms. I have found that recrystallizing this salt tends to purify it from traces of rubidium, for a large quantity

* This method of destroying ammonium chloride is due to J. Lawrence Smith. See Amer. Jour. Sci. (2), xxxiv, 367.

† A description of the acid cæsium nitrates will be published soon from this laboratory.

of the salt which showed no rubidium spectrum, upon systematic recrystallization showed a distinct spectrum for that metal in the final mother-liquor. This, however, is a slow method of purification if it is desired to carry the latter to the last degree, but the nitrate obtained by one or two recrystallizations is pure enough for any ordinary purpose, unless the original antimony salt was contaminated to an unusual extent.

The nitrate is readily converted into carbonate by mixing it with two parts of pure oxalic acid, adding a little water, evaporating to dryness and fusing the residue in a platinum crucible.*

Where the highest degree of purity in a cæsium salt is desired, the salt $CsCl_2I$ † by its recrystallization probably offers one of the best means for accomplishing that object. It is enormously less soluble than the corresponding rubidium, potassium, sodium, and lithium salts. I have found that this salt may be made very conveniently from the nitrate by dissolving one part of the latter together with one atomic proportion of iodine in about ten parts of 1 : 1 hydrochloric acid at a temperature just below boiling. The solution takes place quickly, and, upon cooling, the beautiful yellow salt crystallizes out. It is recrystallized by solution in hot 1 : 1 hydrochloric acid and cooling. One or two recrystallizations, when each crop is well drained and washed with a little cold dilute hydrochloric acid, give, even from impure materials, a remarkably pure product. From this trihalide by ignition, best at a very gentle heat so that the mass does not fuse, pure cæsium chloride may be prepared.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

* Method of J. Lawrence Smith, loc. cit.

† Amer. Jour. Sci. (3), xliii, 17.

ON THE ACID NITRATES.

By H. L. WELLS and F. J. METZGER.

A number of years ago, it was noticed by one of us that when cæsium nitrate is evaporated with strong nitric acid, the last part of the acid is expelled with some difficulty, and the probable existence of a rather stable acid nitrate suggested itself. Mr. A. P. Beardsley, of this laboratory, undertook an examination of the matter last year, and, upon dissolving cæsium nitrate in hot nitric acid of sp. gr. 1.42 and cooling, obtained beautifully crystallized crops of the salt $HNO_3.CsNO_3$. The circumstances were such that Mr. Beardsley's work in this direction was interrupted, and we have undertaken a further examination of the subject. Ditte* has described the following list of acid nitrates:

$KNO_3.2HNO_3$
$NH_4NO_3.HNO_3$
$NH_4NO_3.2HNO_3$
$[2RbNO_3.5HNO_3]$
$[TlNO_3.3HNO_3]$

The two formulæ enclosed in brackets do not correspond to the others nor to the cæsium salt mentioned above, and we have found that they are incorrect. In making these alleged compounds, $2RbNO_3.5HNO_3$ and $TlNO_3.3HNO_3$, Ditte saturated "monohydrated" nitric acid (the liquid corresponding to the formula HNO_3) with the normal nitrates and then simply analyzed the *solution*. He had prepared the other acid nitrates in the same way, but in these cases, having performed the operation above their melting-points, he was able to make definite compounds, and showed that the solutions became perfectly solid at definite temperatures.

* Ann. de Chim. (5), xviii, 320 (1878).

We have easily succeeded in crystallizing two cæsium and two rubidium acid nitrates, and a single thallium salt, and find that the salts of the last two metals do not correspond to the formulæ given by Ditte. We have confirmed the composition of his potassium acid nitrate, and since his ammonium salts correspond exactly to the cæsium and rubidium compounds, we assume that they are correct. Our revision and additions lead to the following list of acid nitrates:

. . . . .	$KNO_3.2HNO_3$
$NH_4NO_3.HNO_3$	$NH_4NO_3.2HNO_3$
$RbNO_3.HNO_3$	$RbNO_3.2HNO_3$
$CsNO_3.HNO_3$	$CsNO_3.2HNO_3$
. . . . .	$TlNO_3.2HNO_3$

These salts belong to two types, of which the diacid form is evidently most readily produced, since thallium and potassium apparently do not yield the other. The cæsium salts are more easily prepared and are more stable than the others.

It has been supposed that "monobasic" acids are incapable of forming acid salts, and it is evident that this belief prevails at the present time, for the following statement is made in a recently published text-book: "Acids like hydrochloric and nitric acids have not the power to form acid salts. They are called *monobasic acids.*" This statement seems to be too sweeping, for there are many acid chlorides, some of which are well known and remarkably stable; in fact, their stability when in solution apparently leads to the opinion that they are not real acid salts. The following list will serve as examples of these compounds: $2HCl.PtCl_4$; $HCl.AnCl_3$; $2HCl.SnCl_4$; $HCl.ZnCl_2.2H\,O$; $2HCl.CuCl$; $2HCl.CuCl_2$; $5HCl.SbCl_5.10H_2O$. Iodides and bromides are also known, for example, $2HBr.SnBr_4$ and HI.AgI. The ease with which hydrofluoric acid forms acid salts is remarkable, and many acid salts of univalent organic acids, such as acetic, propionic, and valerianic acids are well-known. Since it is now shown that the acid nitrates are well defined and in some cases comparatively stable bodies, the old idea that only "polybasic"

acids are capable of forming acid salts should be entirely abandoned. The circumstance that acid nitrates are not more numerous is doubtless connected with the fact that double nitrates in general are rare.

Method of Preparation. — The monoacid salts $RbNO_3.HNO_3$ and $CsNO_3.HNO_3$ are readily prepared by saturating nitric acid of sp. gr. 1.42 with the normal nitrates at a gentle heat and cooling to crystallization. The use of a freezing mixture, such as ice and salt, is desirable in making the rubidium compound, but it is not necessary for the cæsium salt. Only normal potassium nitrate and thallous nitrate could be crystallized from nitric acid of this strength.

The diacid salts $KNO_3.2HNO_3$, $RbNO_3.2HNO_3$, $CsNO_3.2HNO_3$, and $TlNO_3.2HNO_3$ were all prepared by dissolving the normal nitrates to saturation in nitric acid of sp. gr. 1.50 and cooling with a freezing mixture, usually considerably below 0°. In preparing the thallous compound warming must be avoided, because it causes the oxidation of a part of the thallium to thallic nitrate. When this has happened, we find that the addition of alcohol, after the removal of most of the strong nitric acid by evaporation, is a convenient means of converting thallic nitrate into the thallous salt.

Properties. — The monoacid salts $RbNO_3.HNO_3$ and $CsNO_3.HNO_3$ form large, flat masses of small, colorless, transparent crystals, apparently octahedra, arranged in parallel position. The diacid salts $RbNO_3.2HNO_3$ and $TlNO_3.2HNO_3$ form beautiful, colorless, transparent needles, while $CsNO_3.2HNO_3$ forms large, thin, colorless, transparent plates.

All the acid nitrates give off nitric acid more or less rapidly upon exposure to the air at ordinary temperature. The salt $TlNO_3.2HNO_3$ must be dried on paper in a very cool place, as its melting-point is below the ordinary temperature. $RbNO_3.2HNO_3$ decomposes rapidly, and this also must be prepared for analysis in a cool place. The salt $RbNO_3.HNO_3$, and the two cæsium salts, are more stable than the others; the monoacid salts are almost stable in the air, and may be preserved indefinitely in hermetically sealed tubes.

The melting-points of the acid nitrates, as given by Ditte and found by ourselves, are as follows:

$NH_4NO_3.HNO_3$	9° (Ditte)
$RbNO_3.HNO_3$	62°
$CsNO_3.HNO_3$	100°
$KNO_3.2HNO_3$	−3° (Ditte)
$TlNO_3.2HNO_3$	Undetermined
$NH_4NO_3.2HNO_3$	18° (Ditte)
$RbNO_3.2HNO_3$	39–46°
$CsNO_3.2HNO_3$	32–36°

The melting-points of the rubidium and cæsium monoacid nitrates are sharp, but the corresponding diacid salts melt gradually, evidently on account of decomposition. The salt $TlNO_3.2HNO_3$ melts below the ordinary temperature, but its exact melting-point was not determined.

Analyses. — The acid nitrates are very easily analyzed. The amount of normal nitrate was determined by simple heating, and the amount of nitric acid by titration. The following analyses were made with separate crops of the different compounds:

Monoacid Rubidium Nitrate, $HNO_3.RbNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	30.00	30.51	...	30.18
$RbNO_3$	70.00	...	70.43	...

Monoacid Cæsium Nitrate, $HNO_3.CsNO_3$.

	Calculated.	Found. I.	II.	III.	IV.*
HNO_3	24.42	24.23	24.13	...	24.28
$CsNO_3$	75.58	...	...	76.48	75.52

Diacid Rubidium Nitrate, $2HNO_3.RbNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	46.15	45.79	...	...
$RbNO_3$	53.85	...	53.74	53.44

* Determinations by H. P. Beardsley.

Diacid Cæsium Nitrate, $CsNO_3.2HNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	39.25	39.23	39.86	. . .
$CsNO_3$	60.75	. . .	. . .	61.22

Diacid Thallous Nitrate, $TlNO_3.2HNO_3$.

	Calculated.	Found. I.	II.	III.
HNO_3	32.14	33.13	33.02	. . .
$TlNO_3$	67.86	. . .	. . .	67.00

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

INVESTIGATIONS ON DOUBLE NITRATES.

I. Cæsium Double Nitrates.

By H. L. WELLS and A. P. BEARDSLEY.

Comparatively few double nitrates have been described, and it is a curious circumstance that most of these are compounds of metals of the rare-earth group, as follows:

$2KNO_3.Ce(NO_3)_3.2H_2O$
$2NH_4NO_3.Ce(NO_3)_3.4H_2O$
$2NH_4NO_3.La(NO_3)_3.4H_2O$
$2NH_4NO_3.Di(NO_3)_3.4H_2O$

$3Mg(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Zn(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Mn(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Co(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Ni(NO_3)_2.2Ce(NO_3)_3.24H_2O$
$3Mg(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Zn(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Mn(NO_3)_2.2La(NO_3)_3.24H_2O$
$3Ni(NO_3)_2.2La(NO_3)_3.36H_2O$
$3Zn(NO_3)_2.2Di(NO_3)_3.60H_2O$
$3Ni(NO_3)_2.2Di(NO_3)_3.36H_2O$
$3Co(NO_3)_2.2Di(NO_3)_3.48H_2O$

$2KNO_3.Ce(NO_3)_4.1\frac{1}{2}H_2O$
$2NH_4NO_3.Ce(NO_3)_4.1\frac{1}{2}H_2O$

In addition to the above, the only normal double nitrates that have been found mentioned in the literature are the following:*

* There are known, however, certain easily fusible mixtures of nitrates, such as potassium and lead nitrates, and thallous and silver nitrates, but apparently these do not form definite, crystallized compounds.

$KNO_3.Au(NO_3)_3$
$2KNO_3.Tl(NO_3)_3.H_2O$
$2NH_4NO_3.HgNO_3.2\frac{1}{2}H_2O$
$NH_4NO_3.AgNO_3$
$KNO_3.AgNO_3$
$3KNO_3.AgNO_3(?)$

With the exception of the auric and thallic salts, these are all compounds of an alkaline nitrate with a univalent nitrate. It appears to be a singular fact that no double nitrates of alkaline and bivalent metals are known to exist.

Since cæsium is known to form double salts with great facility, we have attempted to prepare double nitrates of this metal with several bivalent metals which generally form double salts very readily. For this purpose we selected lead nitrate, cobalt nitrate, and mercuric nitrate, but after the most careful work we were unable in either case to obtain any definite crystallized product, except crops of the simple nitrates: In each case there was evidence of combination from the fact that solutions were obtained which were much too concentrated to hold in solution the cæsium nitrate that was present, if it had been uncombined. We conclude, therefore, that double nitrates were formed in solution in these cases, but that they were so exceedingly soluble that they could not be crystallized.

It seemed desirable to find if trivalent nitrates, other than those of the rare-earth metals, are capable of forming double nitrates with cæsium nitrate. For this purpose we selected ferric nitrate, and succeeded, although with some difficulty, in preparing a double nitrate.

Cæsium Ferric Nitrate, $CsNO_3.Fe(NO_3)_3.7H_2O$. — This salt is formed at a rather low temperature in very concentrated solutions containing nitric acid and nearly equal molecular proportions of the component salts. It forms pale yellow, deliquescent, prismatic crystals, which melt, not sharply, at 33°–36°. The following analyses were made with separate crops:

	Calculated for $CsNO_3.Fe(NO_3)_3.7H_2O$.	Found. I.	II.	III.
Cæsium nitrate . .	34.64	. . .	35.51	34.87
Ferric nitrate . .	42.98	42.29	42.73	42.68
Water	22.38	. . .	. . .	22.92
Nitrogen	9.94	. . .	. . .	9.54

II. Cæsium Bismuth Nitrate, $2CsNO_3.Bi(NO_3)_3$.

By G. S. JAMIESON.

As a continuation of the investigation just described, experiments have been conducted with cæsium nitrate and bismuth nitrate. The two salts were dissolved in widely varying proportions in dilute nitric acid, and the solutions were evaporated until crystallization took place on cooling. When $2\frac{1}{2}$ or more molecules of cæsium nitrate to 1 molecule of bismuth nitrate were present, the simple cæsium salt crystallized out; on the other hand, when the ratio of cæsium to bismuth was less than about $1\frac{1}{2}$ to 1, bismuth nitrate was obtained. Between these limits a double salt was produced, particularly upon agitating the cold solution, in the form of colorless, prismatic crystals which are stable upon exposure. These were sometimes more than a centimeter in length. The salt melts at 102°. Two crops gave the following analyses:

	Calculated for $2CsNO_3.Bi(NO_3)_3$.	Found. I.	II.
Cæsium nitrate . . .	49.75	47.00	51.22
Bismuth nitrate . . .	50.25	52.63	48.16

The analyses do not agree very satisfactorily with each other or with the calculated numbers. This was doubtless due to the syrupy nature of the mother-liquor which made the drying of the crystals by means of filter paper a difficult matter. The appearance of the crystals, in being homogeneous and different from the separate nitrates, however, leaves no doubt that this is a definite double nitrate.

III. Thallous Thallic Nitrate, $2TlNO_3.Tl(NO_3)_3$.

By F. J. METZGER.

When thallous nitrate is dissolved in concentrated nitric acid (sp. gr. 1.50) by the aid of heat, a part of the salt is oxidized to thallic nitrate, and, upon cooling the properly concentrated solution, large, colorless, transparent, prismatic crystals are formed. The salt is very stable in dry air, but blackens when exposed to moisture. It melts at 150°. Several crops, made under different conditions, were analyzed.

	Calculated for $2TlNO_3.Tl(NO_3)_3$.	Found. I.	II.	III.
Thallic nitrate . .	42.30	43.12	43.13	. . .
Total thallium . .	66.37	65.30	65.53	65.30

The thallic nitrate was determined by titrating the iodine set free by the salt from potassium iodide solution. The total thallium was weighed as iodide.

Conclusions. — No evidence has been obtained that alkaline nitrates form crystallizable double nitrates with the nitrates of bivalent metals.

Several trivalent nitrates, other than those of the rare earth metals, are capable of forming double nitrates.

Sheffield Scientific School,
April, 1901.

ON CÆSIUM PERIODATE AND IODATE-PERIODATE.

By H. L. WELLS.

THE two salts to be described were obtained as the result of an attempt to make a thorough investigation of the cæsium salts of periodic acid. In view of the well-known complexity of periodates in general, it was expected that a considerable number of cæsium periodates would be found, and it was hoped that they might be of much theoretical interest. As a result, however, only normal cæsium periodate, $CsIO_4$, was obtained when cæsium carbonate was added in widely varying proportions to solutions of periodic acid. This was so disappointing that experiments upon the addition of periodic acid to cæsium hydroxide solutions, which were originally planned, were not carried out.

Preparation of Periodic Acid. — The principles involved in the method used for this purpose are not new, but as some of the details may be of use to others, a brief description of the process is given. 12.7 g. of iodine are put into a 10 per cent solution of 60 g. of sodium hydroxide. The liquid is heated to boiling in a flask, and a rapid stream of chlorine gas is passed into the continually boiling solution until the large amount of precipitate suddenly formed begins to cause bumping, when the flame is instantly removed, and the stream of chlorine is continued until no further increase is observed in the white precipitate of $H_3Na_2IO_6$. While the liquid is still warm the precipitate is collected on a Büchner funnel and then thoroughly washed with cold water. It is dried in a steam-bath. The yield is usually about 22 g. or 80 per cent of the theoretical. The sodium periodate is suspended in a large volume of water, three molecules of silver nitrate in solution

are added, the liquid is boiled, filtered hot, and the black precipitate of Ag_3IO_5 is washed thoroughly with water.* The black silver periodate while still moist is suspended in a small amount of water, and chlorine gas † is passed in persistently, with agitation, until the precipitate has become nearly white. The silver chloride is removed by filtration, the liquid is concentrated on the water-bath, then brought to crystallization over sulphuric acid. After being drained, the beautiful crystals of periodic acid are ready for use.

Cæsium Periodate, $CsIO_4$. — This salt crystallizes in white plates, and is rather sparingly soluble in cold water. It was formed upon adding small quantities of cæsium carbonate to concentrated solutions of periodic acid, and also when larger quantities, up to an excess of cæsium carbonate, were used. It can be recrystallized readily by dissolving in hot water and cooling. When a very large excess of cæsium carbonate was added to a solution of the salt and the mixture was evaporated to the point of crystallization, more or less cæsium iodate, $CsIO_3$, usually was formed on account of an accidental or perhaps spontaneous reduction, but no evidence of the existence of any other periodate was thus obtained. The following analyses of six separate crops were made, most of them for the purpose of identification:

	Calculated for $CsIO_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Cæsium . .	41.05	42.02	40.37	. . .	. . .	. . .	. . .
Iodine . .	39.20	. . .	38.19	. . .	. . .	. . .	. . .
Oxygen . .	19.75	19.62	19.77	19.61	19.45	19.65	19.20

Cæsium was determined by treating the substance with concentrated sulphuric acid, evaporating, converting into normal

* The filtrate contains a considerable amount of periodate which is kept in solution by the nitric acid set free by the reaction. Most of this may be recovered in the form of the golden yellow salt $H_3Ag_2IO_6$ by evaporating the liquid to very small volume and cooling, or after evaporating to dryness on the water-bath another crop of Ag_3IO_5 may be obtained by treatment with water.

† According to my experience chlorine is much better than bromine for this purpose.

sulphate by ignition in air containing ammonia, and weighing. Iodine was determined as silver iodide after reduction with sulphurous acid solution. Oxygen was determined by titrating with sodium thiosulphate the iodine set free by the substance in a solution of potassium iodide in the presence of an acid.

Acid Cæsium Iodate-Periodate, $HCsIO_3IO_4.2H_2O$. — This curious salt was first noticed as having crystallized after spontaneous evaporation from a solution of cæsium periodate in dilute periodic acid, in which the periodate had suffered partial reduction. A second crop was purposely prepared from a similar solution, and a third product was made by dissolving cæsium iodate and periodate in dilute periodic acid and cooling. It forms beautiful, slender white prisms. The three crops gave the following results upon analysis:

	Calculated for $HCsI_2O_7.2H_2O$.	Found.		
		I.	II.	III.
Hydrogen	0.19	. . .	. . .	. . .
Cæsium	24.80	. . .	24.00	. . .
Iodine	47.39	. . .	47.38	47.11
Oxygen	20.90	20.75	20.58	. . .
Water	6.72	. . .	. . .	. . .
	100.00			
Iodine as I_2O_5 . .	23.69	. . .	. . .	23.20
Iodine as I_2O_7 . .	23.69	. . .	. . .	23.91

Iodic acid was determined by dissolving the substance in dilute nitric acid, precipitating silver iodate by the addition of silver nitrate, and weighing the silver iodide resulting from its ignition. The periodic acid left in the filtrate from the silver iodate was reduced by the addition of sulphurous acid, and the iodine was determined as silver iodide.

ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.*

By JAMES LOCKE.

I. The Insufficiency of the System as applied to Compounds.

The problems set before the inorganic chemist by the periodic system, which have directly or indirectly guided almost all the inorganic investigations of the past thirty years, may be divided, roughly in the abstract but very sharply in the results obtained, into two classes. The one, of the fruitfulness of which no one can complain, deals with the superficial group-relations which exist between the members of the various families. Their solution leads to what may be called the development of group analogies. The problems of the second class, on the other hand, have either been entirely neglected, or their study has yielded only the most unsatisfactory results. These have had to do with the contradictions of fact which the system, as formulated by Mendeléeff, involved, and to which the system should in course of time adapt itself. But all the more important inconsistencies which it presented in the year 1870 still remain, and are finally recognized as facts which, for the sake of a convenient principle, must not be forced into a conspicuous position. The behavior of the elements of low atomic weight, the appearance of one and the same element in more than one degree of oxidation, the properties of the platinum metals, either receive no expression in the system, or they stand in direct contradiction to its laws. The difficulties involved, however, are confined chiefly to the compounds. The relations between the elements, *as elements*, are in almost every case clearly pointed out in the

* Amer. Chem. Jour., xx, July, 1898.

usual tables. This is true in regard to both the physical and chemical properties of the elements themselves. In this paper, therefore, only that part of Mendeléeff's law will be discussed, which says that the *nature of the compounds of an element is also a function of its atomic weight.*

Of the sixty-five elements having places in the system, nine of them, iron, cobalt, nickel, and the platinum metals, are put in a vertical row by themselves, where they form the so-called eighth family, a family which may be said to fall outside the system proper. In this group many of the regularities which can be traced through other families are wanting.

The valency of the elements increases by one in each successive vertical row of the system, until the fourth is reached, after which each family yields two series of compounds, the one of increased, the other of decreased valency. In the potassium-nickel series, for instance, the various elements should enter into compounds with the valencies:

$$K^{I}, Ca^{II}, Sc^{III}, Ti^{IV}, V^{V}, Cr^{VI}, Mn^{VII}, (F \quad Co, Ni)^{VIII}.$$
$$V^{III}, Cr^{II}, Mn^{I}.$$

So, since chromium falls within the sixth family, the greatest weight is laid upon the fact that chromic acid and its salts show such close analogy to sulphuric acid and the sulphates. The fact that potassium permanganate is isomorphous with the perchlorate, and like the latter only sparingly soluble in cold water, likewise assumes the utmost importance. If compounds of iron, cobalt, and nickel were known, in which these elements were octavalent, they, too, would possess the greatest theoretical value. But, with the exception of nickel carbonyl, a doubtful case of octavalency, these theoretically necessary compounds have never been obtained. Up to the present no one has succeeded in getting beyond the ferric acid of hexavalent iron.

That the decrease in valency, on the other hand, must stop before the eighth family is reached, is obvious, for the seventh family is itself univalent, and a further decrease would prevent iron, cobalt, and nickel from forming any compounds at all.

But this regularity ceases still further on, — with chromium. No univalent manganese compounds have been obtained. Now, inasmuch as the iron, cobalt, and nickel compounds fail to conform with a regularity which can otherwise be traced throughout the entire system, they are assigned an entirely different rôle from that of other elements. They form transition stages, so to speak, from the manganous salts to the copper compounds of the next horizontal row. But this transition is not from the compounds of univalent manganese to those of univalent copper. Univalent manganese is unknown. It is from divalent manganese to divalent copper — to copper in a degree of oxidation which in no way corresponds to the position of this element in the system, and the salts of which have nothing more in common with the cuprous compounds than has sulphuric acid with hydrogen sulphide; the same element can be obtained from both. And even then the road is by no means a smooth one, for directly before manganese stands chromium, and since divalent manganese has no place in the system, the chromous salts must be regarded as the true starting-point for the transition. But the transition from the unstable divalent and stable trivalent derivatives of chromium to those of ferrous and ferric iron is through a manganese in which the relative stability in the two degrees of oxidation is exactly the reverse.

I know I lay myself open here to the charge of expecting too much from the system. But why? Here is a great law of nature, the correctness of which no one can doubt. But in order to illustrate this law, an empirical arrangement of the elements is formed, and this arrangement we are all too apt to confuse with the law itself. The periodic system is satisfactory enough for the elements. Lothar Meyer's curves of the atomic volumes and melting-points prove this. For the compounds it is *unsatisfactory*. And in order to find out how the law does apply to compounds, we must sift out and discuss the discrepancies which the system shows in regard to them.

As with iron, cobalt, and nickel, so it is with all the other

members of the eighth group. These metals, at the time of the promulgation of the periodic system, were assigned a position which, satisfactory though it was in illustration of their properties as elements, was in regard to their compounds absolutely abnormal; and no amount of investigation and speculation, with the periodic system as a basis, can clear up the contradictions which their position entails.

A second point upon which no light has been thrown lies in the behavior of the so-called "typical elements." These, as Ostwald remarks, instead of being types of the families at the head of which they stand, have in the majority of cases properties directly at variance with those of the other members of their respective groups. In his "Principles of Chemistry" Mendeléeff says: "The elements of the first two series have the least atomic weights, and in consequence of this very circumstance, although they bear the general properties of a group, still they show many peculiar and independent properties. These lightest elements are:

H;
Li, Be, B, C, N, O, F·
Na, Mg, . ., . ., . .."

As Mendeléeff left these elements, "typical," so they have remained, and the history of thirty years contains no mention of a successful attempt to unite them more closely than by that ill-fitting word to the groups to which they should show analogies.

Lithium is the lightest of all the elements having places in the system. It should, therefore, from the above, have the greatest number of independent properties of any of the typical elements. Or, one should at least expect to find metallic lithium and lithium compounds varying from the higher alkali metals and their derivatives in one and the same degree, since their departure from the rest of the group is conditioned by one and the same cause. The abnormal behavior of the other typical elements should be along the same lines as in the case of lithium and its compounds. The essential properties

of metallic lithium stand in strictest analogy to those of the other alkali metals. Metallic beryllium fits in accurately in the series formed by magnesium, zinc, cadmium, and mercury. Between boron and aluminium the analogy is less clear; but it appears again in full force in the properties of free carbon and silicon. The two elements show, in their physical properties, allotropic modifications, and indifference to reagents, the strongest similarity. Fluorine and chlorine, in the elementary state, present the most striking analogies; and the gradations in character which the free halogens undergo with increasing atomic weight, from fluorine through to iodine, yield one of the most perfect chemical series imaginable.

Of the seven elements making up the first horizontal row, therefore, at least four possess, *in the elementary state*, properties closely akin to those of the subsequent elements in their respective families, and complete the series which the latter form.

Now, if the periodic system is true for compounds as well as for the elements themselves, then the compounds of analogous elements must be analogous, — a simple deduction from the law which is not altered in its bearing by the fact that the elements with which we happen to be dealing fall within the so-called typical class. If the low atomic weights, therefore, of the four elements — lithium, beryllium, carbon, and fluorine — are not of such influence as to prevent their ranking as they should in their respective families, we must expect that their compounds will also show analogy to those of the other members of their groups. The compounds of lithium vary more or less from those of the other alkali metals, it is true; its phosphate and carbonate, especially, are less soluble; but, nevertheless, the lithium salts in general possess the characteristics of alkali derivatives, to an extent which would certainly prevent any one from considering lithium as anything but an alkali metal. Carbon and silicon likewise bear close relationship in their compounds. The property of carbon which gives rise to organic radicals and the existence of such a multitude of combinations between but a few elements, the

ability of the carbon atoms to unite with one another, likewise appears in silicon. The silicon hydrides, the various chlorides, bromides, and iodides, silicon-chloroform, and the complex oxygen compounds, such as silico-oxalic and mesoxalic acids, illustrate fully the strong similarity between the influence of tetravalent carbon and that of silicon upon their compounds.

The law, and its expression by the periodic system, therefore, holds good in the case of lithium and carbon, and no fault can be found with the typical behavior of the two elements. Now, if the effect of small atomic weight upon both lithium and carbon is too slight to cause in the nature of their compounds any great variation from that of their homologues, one has a perfect right to assume that this separating influence will not be greater in an element which in its atomic weight lies between the two; but, after a comparison unprejudiced by the fact that an analogy between the compounds of beryllium and magnesium is required by their positions in the system, can a single trace of true resemblance be found between them, or between beryllium derivatives and those of any other element in the second vertical row? Magnesium hydroxide and beryllium hydroxide are both dibasic, it is true. But there the similarity ceases.

A strongly distinctive feature of all magnesium, zinc, and cadmium salts is seen in their behavior toward ammonia and ammonium salts. They also have a pronounced tendency to form double salts with the compounds of other metals. Their oxides are insoluble in water, but soluble even in weak acids. Calcium, strontium, and barium, on the other hand, are characterized by their soluble, strongly alkaline hydroxides, by their difficultly soluble sulphates, and by the difficulty with which they enter into double salts. These are group characteristics, the presence of any one of which indicates the others. They give a tone to, and define the nature of, all the compounds of the two series. But to beryllium salts not one of them applies. Similar to magnesium though the metal be, its compounds show perfect indifference to ammonium salts;

they form no double salts,* and the oxide is practically insoluble even in strong, hot acids; as little soluble, in fact, as alumina. This last fact, together with the ready solubility of the sulphate and of the fluoride, and the insolubility of the sulphide, etc., prevent any comparison of the beryllium compounds with those of the alkaline earths.

With fluorine, the nature of the compounds of which it will be unnecessary to discuss in full, the case is similar, although its atomic weight is nearly three times as great as that of lithium. The properties of the free element show it to be a pronounced halogen, with characteristics which one would expect to find in a halogen of lower atomic weight than chlorine. But its compounds are not only widely different from those of chlorine, but they often vary in a direction contrary to that of the gradations observed in the rest of the series. Fluorine, it is true, forms in common with the other halogens an acid of the type HR. But in distinction from hydrochloric, hydrobromic, and hydriodic acid, hydrofluoric acid has a remarkably low molecular conductivity; and its salts, in the majority of cases, have properties which are directly the opposite of those of the chlorides, bromides, and iodides. The most pronounced chemical characteristic of the halogen acids certainly lies in the solubility of their salts with heavy metals, and the insolubility of the silver, cuprous, and mercurous compounds. The *fluorides* of silver and mercury, on the other hand, are readily soluble: those of calcium, strontium, barium, magnesium, manganese, iron, cobalt, nickel, chromium, cadmium, copper, bismuth, lead, and others, are either sparingly soluble, or dissolve only in an excess of hydrofluoric acid. In the readiness with which fluorine enters into metallofluoric acids is seen another great distinction from the other halogens. In this, as in many of its other properties, it approaches very closely to cyanogen. Hydrofluoric and hydrocyanic acids and

* Certain double fluorides must be noted as exceptions to this statement. The double sulphates, phosphates, etc., known, may be disregarded, as they can be represented by simple constitutional formulas, and this formation is of less significance than that of double halogenides and the like. Both calcium and strontium yield double sulphates.

their salts have, in fact, little more in common with hydrochloric, hydrobromic, hydriodic acids, and the halides, than the fact that they are monobasic or derivatives of monobasic acids.

We have, therefore, in lithium, beryllium, carbon, and fluorine, four typical elements which in the free state, *as elements*, stand in close relationship to the other elements of their respective groups. In two of them, lithium and carbon, the influence of their low atomic weights is not such as to deprive their compounds of the chemical nature which characterizes the derivatives of their analogues. The others, although one of them lies *between* lithium and carbon, and the other has an atomic weight almost large enough to take it out of the typical class, fail to show analogy to their homologues; that is, to satisfy the requirements of the system, as soon as they pass from the free state into combination.

These are contradictions which even the mysterious influence of a low atomic weight will not explain. They were known in 1870, and they stand to-day. With the development of organic chemistry, and the increase in the number of bodies known, which could not be explained by the laws of valency alone, stereochemistry appeared. Molecular compounds have been the subject of numerous theories, of which one at least, that of Werner, promises to bear fruit; but the inconsistencies shown, in reference to the other elements, by those of low atomic weight, the exceptions to a law more far-reaching than that of valency itself, have remained untouched, simply in recognition of the fact that it was hopeless to look for any explanation for them which could be reconciled to the system. And why? Because the inorganic chemist, in standing upon the periodic system, has been unable to dissociate in his mind the chemical compound from the elements of which its formula contains the symbols.

Of the work done in the development of group analogies, little need be said. This has been the only successful field of investigation which the formulation of the system opened. But it may be well to point out briefly certain inconsistencies

which are involved in the development of these analogies between neighboring metals in the horizontal rows.

One of the pronounced features of the periodic system is the regularity with which the valency of the elements increases in the successive vertical rows, — a regularity to which, in fact, so much importance is attached that Mendeléeff can say without fear of criticism, "PbO_2 is the normal salt-forming oxide of lead, as are Bi_2O_5, CeO_2, TeO_3 of bismuth, cerium, and tellurium!" According to Mendeléeff, when an element forms two series of compounds, as copper, for instance, in one of which it has the same valency as its neighbor in the horizontal row, its compounds in this degree of oxidation must be similar to those of its neighbor. This rule is well illustrated in the case of copper, for the cupric compounds do bear a very close resemblance to those of the next element, zinc. But examine the rule in its full extension. The formation of an alum by any trivalent metal is rightly regarded as characterizing its behavior throughout all its compounds in this degree of oxidation, and sharply distinguishes its sesquioxide from those of another great class of elements, the rare-earth metals. Associated with the formation of alums is the behavior of the cyanides toward potassium cyanide. All the sesquioxides* which form alums yield soluble double potassium cyanides, the great majority of which have the formula $K_3M(CN)_6$.

In the series,

K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni,

the most typical double cyanide is formed by iron; that of cobalt is also stable, and on the other side we find an analogous salt formed by manganese, "owing to its proximity to iron." But chromium, beyond manganese, also forms one; and from some experiments which I myself have made, I find also that potassium vanadicyanide, $K_3V(CN)_6$, is not only capable of existence, but a well-defined compound. We have here the character which the atomic weight 56 lends to the compounds

* The only exception is in the case of aluminium, the cyanide of which is decomposed by water. Potassium cyanide precipitates the hydroxide.

of trivalent iron exerting an influence upon that of one element to the right and three elements to the left. With the alums the case is still more remarkable. These bodies are formed by cobalt, iron, manganese, chromium, vanadium, and titanium; or by six of the ten elements in the row. And not only that; scandium, the metal next to titanium, not only forms a sesquioxide, but this is its only degree of oxidation. Its compounds, however, have the properties characteristic, not of ferric and aluminium salts, but of the rare earths. And, nevertheless, the close proximity of this element to titanium does not lend to the trivalent compounds of the latter a single one of the properties of the rare earths. We must seek the influence to which the character of the titanous salts is due far over at the edge of the table.

In the foregoing pages no attempt has been made to criticise the analogies which exist, in the various series, between the elements themselves. With this feature of the system little fault can be found. The alkali metals, the alkaline earth metals, Be, Mg, Zn, . ., Ge, Sn, Pb, are thoroughly similar among themselves, and well illustrate the gradation in properties with increasing atomic weight. But with the compounds the case is entirely different. The derivatives of typical elements show no regularity — even in their abnormal behavior; the compounds of the eighth group have a decidedly anomalous position. The similarity between the derivatives of elements in states of oxidation uncalled for by the system, either cannot be explained at all, as in the case of lead and barium, magnesium and manganese compounds, or we are forced to ascribe to one or the other series a certain vague, transitive nature. The reason for this lies, not in the principle that the chemical nature of an element and its compounds is a function of its atomic weight, but in our failure to recognize the twofold character of this principle. We attempt to apply one and the same expression of the law to both elements and compounds. But one has no right, in the systematization of one class of substances, to impose upon himself restrictions which arise only from the system which he employs for

another class. No arrangement of the elements according to their atomic weights can be made, which expresses the analogies between the elements themselves, and in which, for instance, magnesium and manganese receive analogous positions. And the result is that, in order to emphasize the relation between zinc and magnesium, which such an arrangement does exhibit, the adherent of the periodic system deliberately closes the door to an explanation of the far closer analogy between the compounds of magnesium and manganese, as if the latter were not conditioned by an equally important law of nature.

A system for the compounds, founded upon the atomic weights of the elements, must also necessarily lead to confusion from another source, for the investigation of the compounds is undertaken solely to characterize the *general chemical nature* of the element. Thus, little distinction is drawn between reactions which do not involve a change in degree of oxidation and those which do. If the two are separated at all, it is only when the resulting compounds are very stable, or else conform to the position of the element in the periodic system. To cuprous compounds, though they are unstable, great importance is attached, because copper belongs to the first family. But, even in so full and scientific a text-book as that of Mendeléeff, the salts of trivalent manganese are reviewed with little more than the passing remark that they somewhat resemble ferric compounds, and that the chloride decomposes when its solution is warmed. The latter fact seems to deprive the manganic salts of all theoretical interest.

But in a comparison between the derivatives of two metals in the same degree of oxidation, the question of *existence* becomes of more importance than stability, for the latter is often dependent entirely upon external conditions. The fact that bromine is liquid, iodine a solid, at ordinary temperatures, does not prevent the most important analogies being drawn between the physical properties of the halogens in the same state of aggregation, though to obtain bromine and iodine as gases, heat must be employed. So it is, with many compounds.



They may perhaps be obtained only under, for us, extraordinary conditions, but their very existence may point out in the constituent elements properties which we should otherwise never expect. As an example of such a case only the newly discovered alums of vanadium need be mentioned. The existence of these bodies shows that in spite of the similarity between phosphates and vanadates, the vanadium atom exerts upon the nature of its trivalent compounds the same influence as does iron upon that of the ferric salts. A vanadic solution absorbs oxygen with great avidity, and is therefore called very unstable, but the presence of oxygen is an arbitrarily imposed condition. If oxygen were a rare element, the trivalent salts of vanadium would probably be regarded as its normal compounds, and a vanadate looked upon very much as we look upon ferric acid to-day.

The chemical behavior of an element in a given degree of oxidation must be characterized along two lines. First, by the study of its compounds as mineralogical specimens, their composition, physical properties, solubility, volatility, and the like, together with the reactions which they show without involving change in the degree of oxidation. Secondly, by its passage from this degree of oxidation into others. The first is, in my opinion, by far the more important, for the properties of the compounds of an element in two different degrees of oxidation differ absolutely from one another; and in the two the element appears in entirely different rôles. It is only after we have ascertained in how far the element can alter its *apparent* character, in corresponding with entirely different elements in different degrees of oxidation, that we can solve its *true* character and find out a general law for its behavior in all its compounds; and this can be ascertained only by a careful comparison of its compounds with those of other elements in the same degree of oxidation.

A classification based upon this principle, of course, presents great difficulties, owing to the very unsatisfactory extent to which the elements in their unstable degrees of oxidation have been investigated. A thorough study of the compounds, how-

ever, has shown that it is capable of giving most interesting results.

II. Gradations in the Properties of Alums.*

In my first paper on this subject,† I attempted to show that the well-known difficulties which confront the chemist in classifying the elements and their compounds according to the Periodic System are confined practically to the latter class of substances. That there is a definite connection between the properties of an element and those of its compounds is of course obvious, from the numerous cases in which both fulfil the requirements of the system. But, to take one of the chief difficulties, there are almost no instances in which, when an element can appear in more than one degree of oxidation, the properties of its compounds in each type find accurate interpretation by the System. As a case in point may be cited nitric acid, the nitrates, and nitrous acid and the nitrites, as compared respectively with the derivatives of the pentoxide and trioxide of phosphorus. So far as their oxygen compounds are concerned, the two elements have in neither the quinivalent nor trivalent state anything in common, except their valence and acid-forming nature. In crystallographic form, solubility, even in formulas, their derivatives are inherently different. Nitrogen pentoxide is a volatile liquid; phosphorus pentoxide a non-volatile solid. The former forms only the monobasic acid HNO_3; the latter yields preferably polybasic acids; the normal nitrates are in every case readily soluble in water: the normal phosphates, pyrophosphates, and metaphosphates are in almost every case insoluble in water.

With the trioxides the degree of similarity is about the same; strict analogy is practically absent. But nevertheless such a loose periodic-system worship prevails, that almost every modern text-book on inorganic chemistry contains a stereotyped statement that nitric acid is analogous to phosphoric acid. In some instances even these bounds have been

* Amer. Chem. Jour., xxvi, August, 1901. † Ibid., xx, 581.

far overstepped. Probably the most thoroughly systematized smaller work on the subject is that of Professor Ramsay. On pp. 333 ff. of his "System of Inorganic Chemistry" (1891), he classes nitrogen tetroxide with vanadium tetroxide, nitrous acid, and with vanadious hydroxide. The latter two are apparently analogous because they have the analogous formulas NO(OH) and VO(OH). If this is enough for chemical analogy, why should not the aluminium compound, AlO(OH), be put in the same class? Aluminium and vanadium both form alums, and, as he emphasizes of vanadium hydroxide, both unite with the alkalies. I speak of this, not in criticism of Professor Ramsay's book, but in protest against the all-prevailing tendency to go a-begging for chemical analogy when the system requires it.

The term "chemical character of an element" has two very different meanings. In the first place it denotes the behavior of the element itself, in the free state; in the second, the type of reactions of its compounds. In the latter case we may perhaps use an explanatory prefix, and say, for instance, "the character of *ferric* iron" or of "*ferrous* iron." The two terms denote two absolutely different states of matter. When one speaks of ferric iron, the mind involuntarily associates it, not with ferrous iron, nor metallic iron, but with the salts of aluminium and trivalent chromium; with two elements which in the free state bear no analogy to metallic iron,* and no relation between which and iron is shown by the System. The simplest and most natural analogues of ferric iron are merely the trivalent ions of aluminium and chromium. On the other hand, "ferrous iron" brings to the mind, in addition to the idea of something readily oxidizable, the thought of magnesium and zinc compounds, — derivatives of elements which again have nothing in common with metallic iron, and also no resemblance to the metals which iron in the trivalent state is analogous. Unless a very strong distinction is made between

* By this I mean the strict analogy which is exhibited between free elements belonging to the same family and sub-group in the System; for example, metallic zinc and cadmium, silver and gold, arsenic and antimony, etc.

the different usages of the term "chemical character of iron," therefore, this brings about a state of hopeless confusion. Up to the present time it certainly has led to a marked subordination, in importance, of compounds containing elements in unstable states of valence to those in which they are stable. Practically, this is all very well. But from the theoretical standpoint it imposes a direct obstacle in the way of careful and systematic interpretation of fact, for it makes in such cases the power of oxidation or reduction much more important than the simple properties of the compounds as such.

The laws of electricity cease to obtain, as soon as that force has been converted into light, or heat, or chemical energy — no matter which. But ferric iron and ferrous iron are just as distinct primary forms of matter as these are distinct forms of energy. Like the latter, they may be converted the one into the other, or they may be converted into metallic iron. But whether a ferric salt passes into a ferrous salt or into metallic iron, *the form of matter analogous to aluminium* in the combined state ceases to exist. What it becomes, and how readily it undergoes alteration, are questions common to *all* the ferric compounds, and should be theoretically regarded as belonging to a set of problems entirely distinct and separate from those involving the individual salts.

In order to clearly characterize an element in a given degree of oxidation, the first step should be, not to ascertain how stable or unstable its compounds are, but how nearly they approach, in their physical properties, solubility, etc., the corresponding salts of other elements of the same valence. Such arbitrary conditions as, for instance, the presence of oxygen in working with easily oxidizable substances, should be avoided. And, furthermore, the question of analogy should be decided along strict lines. The rare-earth metals are, more often than not, spoken of as analogous to aluminium. But the two notable properties which characterize the aluminium salts — the extremely weak basicity of the hydroxide, with the corresponding readiness to form basic salts; and the marked tendency

to form complex ions (still more highly developed in chromium and ferric iron), as illustrated in the behavior of aluminium solutions containing oxalic, tartaric, or other organic acids, are just the reverse of the properties which characterize the strongly basic rare-earths. In Dammer's Handbuch we find specific mention of fourteen derivatives of aluminium chloride. Under cerous chloride — the chlorine compound of the best investigated rare earth — we find but two.* Barium chloride and cupric chloride show a similar difference. In both cases the divergence is due to much the same cause. The very nature of the strongly basic ions of barium and cerium prevent the formation of such derivatives; and since the divergence in the behavior of the chlorides is duplicated in that of sulphates, nitrates, bromides, and countless other salts, it surely indicates a radical distinction in the characters of cerium and aluminium, to which much more weight should be attached than to the fact that the hydroxides of both are flocculent precipitates. The latter resemblance is essentially the basis of assertions that they are analogous. Cerium may be regarded as the prototype of the rare-earth metals; aluminium as that of trivalent chromium, manganese, vanadium, iron, cobalt, and others. In each group the reactions of these typical metals are closely followed by all their respective members, in a way which proves that the separate reactions of each are not to be regarded as individual functions of the elements, but closely correlated with one another. For instance, it means that a trivalent metal which forms alums will yield complex tartrate ions; and that a trivalent metal which has a strongly basic hydroxide will form an insoluble oxalate, and not form an alum nor a double chloride with potassium chloride; but that its oxide will dissolve readily in dilute acids. As illustrations in the above, I have chosen the trivalent metals by chance. Others would have done just as well. If we compare the solubility relations and, exclusive of those in which a change of valence takes place, the reactions, of cuprous compounds, with those of the corresponding silver salts,

* Exclusive of the platinichloride, etc.

we find an almost exact similarity between the two. But to ascertain experimentally in how far the strict classification of the elements in the manner indicated is possible, the trivalent metals are especially suitable. Among the alum-forming elements we find one (cobalt) which in the trivalent state yields compounds that are very unstable because of the high valence; and a second one (vanadium) whose compounds are equally unstable because of the abnormally low valence. The range of atomic weights of the alum-forming trivalent metals, from 27 (Al.) to 114 (In.) is also exceptionally great for an isomorphous series, and these elements constitute members of six out of the eight families in the System.

The total number of trivalent elements entering into the compounds $M^{I}\,M^{III}\,(SO_4)_2.12H_2O$, is nine, — aluminium, titanium, vanadium, chromium, manganese, iron, cobalt, gallium, and indium. Of univalent elements, M^{I} represents five: sodium, potassium, rubidium, cæsium, thallium; and also the ammonium, hydroxylammonium, methylammonium, etc., radicals.* A cursory glance over the literature shows at once that there is a more or less pronounced decrease in stability with increasing atomic weight of the trivalent metal in an alum, and apparently that the heavier the univalent metal, the greater will be the stability. Thus, sodium enters into alums only with the lightest of the trivalent metals, aluminium, vanadium, and chromium. The only stable potassium alums are those of aluminium and chromium: potassium ferric and gallium alums break down into basic salts very readily, and the only double sulphates of potassium and indium which can be obtained have the formulas $KIn\,(SO_4)_2.4H_2O$ and $K_2SO_4.2In_2(SO_4)_3.6H_2O$.

The only alums which have as yet been obtained of titanium are those in which the univalent metal is cæsium or rubidium.† After much doubt had been cast upon the exist-

* The existence of the silver aluminium alum described by Church and Northcote is denied by Retgers.

† Piccini, Zeitschr. für anorg. Chemie, xvii, 355. I have obtained indications of the existence of that of potassium.

ence of the manganese alums described by Mitscherlich, Piccini has shown that at least the cæsium compound of this element can be easily obtained.* Owing to the great instability of their salts, and the correspondingly slight value which could be attached to measurements of their physical constants, I have felt it useless to include these metals in the present investigation, which covers, however, alums of all the other trivalent metals mentioned above, except gallium.

I have also rejected the salts of the substituted amines, as involving the ulterior question of the influence of complex radicals. The ammonium alums, however, in view of their frequent occurrence, have been carefully studied, in order to ascertain how far the generally greater readiness of this complex to yield double salts, as compared with that of potassium, is capable of exact determination. The univalent groups studied, therefore, were sodium, potassium, ammonium, rubidium, cæsium, and thallium. For the necessary rubidium and cæsium material I am indebted to the kindness of Prof. H. L. Wells, who kindly placed some very pure compounds of these metals at my disposal. The salts given in the following table were investigated.

	Al = 27.	V = 51.1.	Cr = 52.1.	Fe = 56.	Co = 59.	In = 113.
23	Na	. .	Na	. .	. .	. .
39	K	K	K	K	. .	. .
. .	NH_4	NH_4	NH_4	NH_4	. .	. .
85	Rb	Rb	Rb	Rb	Rb	Rb
133	Cs	Cs	Cs	Cs	Cs	Cs
204	Tl	Tl	Tl	Tl	. .	. .

Solubility in Water at 25°. — As a criterion of the properties of these compounds, their solubility in water at 25° was first determined. The literature contains data only upon the solubility of the compounds of aluminium † and vanadium, ‡ and all those given seem to be of more or less doubtful character,

* Zeitschr. für anorg. Chemie, xvii, 355; xx, 12.

† Poggiale, A., ch. (3), viii, 467; Setterberg, Liebig's Annalen, ccxi, 100; Mulder, Scheidekund, Verhandl., 1864, 91; etc.

‡ Piccini, Zeitschr. für anorg. Chemie, xiii, 441.

the results having in each case been obtained without the use of a thermostat. In addition to this fact, the actual temperatures chosen by different experimenters for their determinations were rarely identical; so that their results for a given degree would have to be calculated by interpolation. I have accordingly been forced to make new measurements in each case.

The determinations were made in two-ounce bottles, containing water and the finely divided salts in excess. These were placed in a digesting bath as described by Noyes,* and rapidly shaken by means of a turbine for from four to six hours. The bottles were then placed upright in the bath, and the suspended salts allowed to settle for two hours. The temperature of the bath was controlled by a gas regulator, and its variation, in the determinations used below, never exceeded 0.2°. From three to eight cubic centimeters of the supernatant solutions were then transferred by means of a pipette, the bulb of which had been warmed, to small weighing-glasses, weighed, and evaporated to dryness. The amounts of the dissolved salts were then determined by heating for four hours at 200°, at which temperature they became fully dehydrated. The accuracy of this method was first ascertained by experiments made with a variety of alums. In these a weighed quantity of the salt was dissolved in a few cubic centimeters of water, evaporated to dryness, and heated to constant weight. The water was added to ascertain whether an error would be introduced through basic salt formation. The following are some of these determinations:

0.4513 g. $CsCr(SO_4)_2.12H_2O$ gave 0.2858 g. anhydrous salt, calculated 0.2869 g.
0.3540 g. $CsFe(SO_4)_2.12H_2O$ gave 0.2262 g. anhydrous salt, calculated 0.2259 g.
0.2264 g. $CsAl(SO_4)_2.12H_2O$ gave 0.1411 g. anhydrous salt, calculated 0.1403 g.
0.7814 g. $TlCr(SO_4)_2.12H_2O$ gave 0.5473 g. anhydrous salt, calculated 0.5474 g.

* Zeitschr. für physikal. Chemie, ix, 606.

The solubility determination of the vanadium alums required great caution, owing to the readiness with which they undergo oxidation. These salts, which were made according to Piccini's directions,* by electrolysis, were washed by decantation with boiled water containing carbonic acid, in the vessel in which they had been crystallized; and were then brought directly into the bottles, without having been exposed to the air for an appreciable length of time. The water used for their solution had previously been boiled, and carbon dioxide led through it in the bottles. The resulting solutions were in this case analyzed by the titration of weighed quantities according to Browning's method.† The alums of cobalt, of which only the potassium and ammonium compounds had been described hitherto, ‡ unfortunately decompose quite rapidly in solution, giving off oxygen, and determinations could therefore not be made with them. My supply of indium, also, was too small to permit a determination of any but its cæsium alum. The results obtained with this compound alone, however, sufficiently indicate the rôle of indium as an alum-forming element.

The results given below are in about half the cases averages of two or more closely agreeing determinations, and are chosen from the total number made as having been obtained under the most perfect conditions of temperature, etc. The values refer to the number of parts of salt dissolved in one liter of water, and in the successive tables M^I represents the univalent metals contained in the alums of the trivalent metal M^{III}.

M^{III} = Aluminium, At. wt. = 27.

M^I =	Na	K	NH_4	Tl	Rb	Cs
Anhydrous salt,	. .	72.3	91.9	75.0	18.1	4.7
Hydrated salt,	. .	138.4	191.9	117.8	31.5	7.6

M^{III} = Vanadium, At. wt. = 51.1.

M^I =	Na	K	NH_4	Tl	Rb	Cs §
Anhydrous salt,	. .	. .	316.9	256.0	57.9	7.71
Hydrated salt,	. .	. .	785.0	433.1	99.3	13.10

* Zeitschr. für anorg. Chemie, xi, 106.

† Ibid., i, 158. ‡ Soc. Edinburgh, lix, 760.

§ Piccini obtains the same order for the solubility of the vanadium alums

M^{III} = Chromium, At. wt. = 52.1.

M^{I} =	Na	K	NH_4	Tl	Rb	Cs
Anhydrous salt,	. .	125.1	107.8	104.8	25.67	5.7
Hydrated salt,	. .	243.9	212.1	163.8	43.40	9.4

M^{III} = Iron, At. wt. = 56.

M^{I} =	Na	K	NH_4	Tl	Rb	Cs
Anhydrous salt,	Does not exist.	Basic salt separated.	441.5	361.5	97.4	17.1
Hydrated salt,			1244.	646.0	169.8	27.2

M^{III} = Indium, At. wt. = 114.

M^{I} =	Na	K	NH_4	Tl	Rb	Cs
Anhydrous salt,	Does not exist.	Does not exist.	. .	. .	. .	75.7
Hydrated salt,			. .	. .	. .	117.3

The sodium alums known dissolve in much less than their own weight of water, and were therefore unsuitable for exact determinations. A sodium alum of iron could not be obtained. With regard to the effect of the univalent metals upon the solubility, it is seen that the higher the atomic weight of an alkali-metal, the less soluble is its alum with any given trivalent metal. The solubilities of the ammonium and thallium compounds, however, lie between those of the corresponding salts of potassium and rubidium. The salt $NH_4Al(SO_4)_2.12H_2O$ forms the only exception to this rule. It is somewhat more soluble than $KAl(SO_4)_2.12H_2O$.* The thallium alums, furthermore, are in each case somewhat less soluble than those of ammonium.

The key to the effect of the trivalent elements upon the

at 10°. Expressed in parts by weight of the salts dissolved in 100 parts water, his determinations are as follows:

V—K	V—NH_4	V—Tl	V—Rb	V—Cs
198.4	39.76	11.06	2.56	0.464

* In Poggiale's determinations, this ammonium alum was found to be less soluble than the potassium salt. His results for the latter correspond almost exactly with mine for the ammonium salt, and those for the ammonium alum with mine for that of potassium. It is probable that the coincidence is due to a false arrangement of his tables.

solubility relations is given in the failure of any beyond vanadium to form alums with sodium, and in the decomposition of the potassium ferric salt by water. As this would indicate, the solubilities of the alums of the successive trivalent metals with a given univalent metal increase steadily from aluminium to indium. From what one can judge through the literature, gallium alums, also, follow this rule, being, next to those of indium, the most soluble. The chromium alums alone form an exception. Their behavior will be touched upon at a later point.

In the following table I give the solubilities of all the alums determined, expressed in gram-molecules of the anhydrous salts per liter of water:

	M^{I} = K	NH_4	Tl	Rb	Cs
M^{III} = Al	0.28	0.387	0.177	0.059	0.013
V	. . .	1.210	0.573	0.177	0.0204
Cr	0.441	0.407	0.212	0.078	0.0151
Fe	. . .	1.659	0.799	0.293	0.045
In	. . .	. . .	. . .	. . .	0.172

These results may be represented graphically as a function either of the molecular weight of the respective alums of given trivalent metals, which is virtually the same thing as if they were plotted according to the atomic weights of the univalent metals, but introduces the ammonium salts; or they may be referred to the atomic weights of the trivalent metals. To show the influence of both the univalent and trivalent metals, I give in Figs. I. and II. the results obtained by each method. In Fig. I. the solubilities are plotted as functions of the molecular weights, the univalent metal being the variable.

As is seen, the curves are in general of the same nature, but they have no uniformity of position, and render no gradation in the solubilities of the alums visible. This is true whether we include the ammonium salts or not, or, in other words, whether the solubilities be referred to the molecular

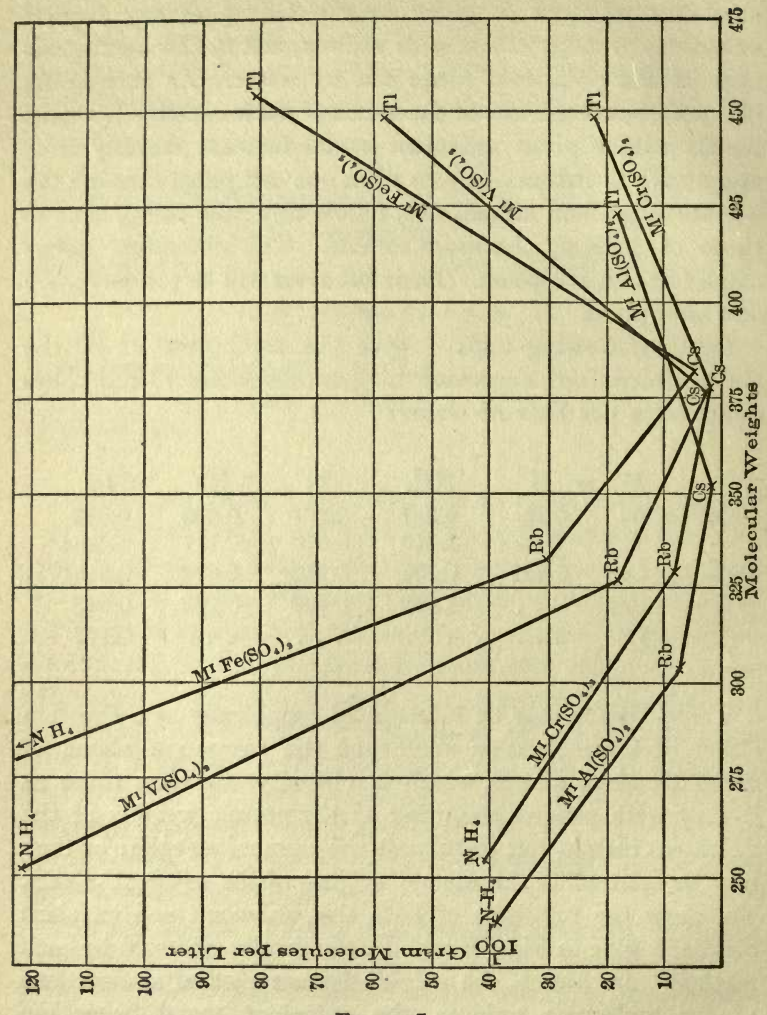


FIGURE I.

weights or to the atomic weights of the univalent metals. *The only influence which the univalent metals or radicals exert is a specific one.* The cæsium salts are in all cases the least soluble, the rubidium salts next, but the comparatively great solubility of the thallous compounds, which, according to the

gradation observed in the case of the compounds of the alkali metals proper, should be the least soluble of all, prevents any satisfactory representation of the solubilities as a function of the atomic weights of the univalent metals.

This specific influence of the univalent metals is readily seen in Fig. II, in which the solubilities are plotted as a function of the atomic weights of the trivalent metals.

As we pass from the cæsium compounds through those of rubidium and thallium to the ammonium alums, the difference in solubility of the successive salts of a given trivalent metal becomes greater. The increase is also the greater, the heavier the trivalent metal; the result being that while the cæsium alums of all the trivalent metals differ only slightly in solubility, and their curve has therefore a nearly horizontal position, the curves of the remaining univalent radicals successively become more inclined; * the whole effect being somewhat like that of an opening fan. But in each case the curves show a sharp break at the chromic compounds; slight in the cæsium curve, but more pronounced with each successive univalent metal. Apparently, since the chromic salts accordingly fail to fall properly within the series of gradations with increasing atomic weight of the trivalent metal, the conclusion might be drawn that the great readiness with which this element forms alums is in the actuality an abnormal property. I believe, however, that this is a very loose way of interpreting the fact. Abnormal things do not occur in nature. In the increasing solubilities of the chromic alums as we pass from cæsium to ammonium, they show exactly the same mutual relations as are shown by the alums of aluminium, vanadium, or iron. They are perfectly normal in everything, except that their behavior is not expressed, like that of the other trivalent metals, by the atomic weight of the metal they contain. And

* Prof. Horace L. Wells suggests to me that the marked difference shown here between the solubilities of the rubidium and cæsium alums of iron might have a practical bearing upon the technical separation of rubidium and cæsium. At present this is usually effected by the fractional crystallization of their aluminium alums. By using the ferric compounds it would probably be much more perfect.

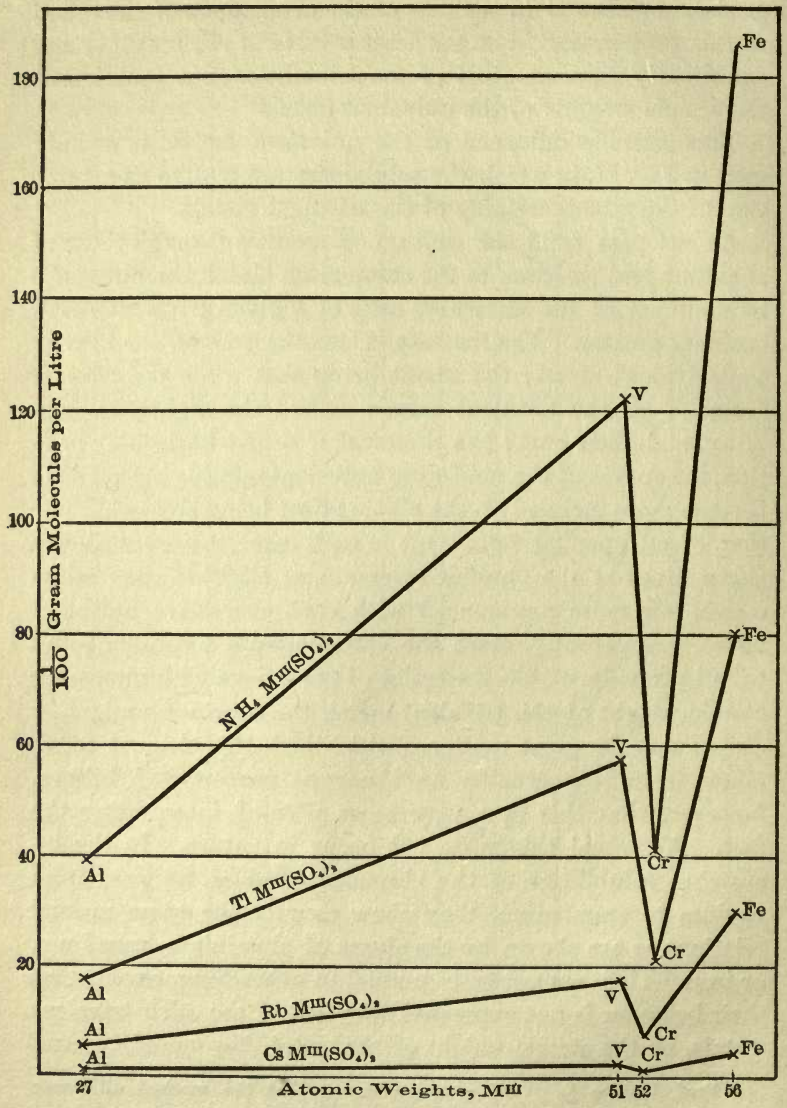


FIGURE II.

this fact indicates almost positively that *the properties of the compounds are not a function of the atomic weight of the element.*

If they were, chromic alums would have about twice their actual solubility.

I do not mean by this to make a sweeping denial of all analogy shown in the Periodic System. Whatever the determining cause of the properties of compounds may be, it is certainly commensurable, in a great many instances, with the atomic weights. But our progress toward the systematization of the compounds will be slow indeed, if we refuse to recognize that Mendeléeff's law is but a slight approximation of the truth. The abnormal behavior of the thallium alums, according to the Periodic System, might be conventionally explained by the position of thallium as extraneous to the first family of the table. But in the case of chromium such an explanation is totally inapplicable. The elements aluminium, vanadium, iron, and cobalt * constitute members of three different families, and nevertheless their alums show a satisfactory gradation according to the atomic weights of these elements. Their alums are merely intermediate members in the series of which the end members, the aluminium, gallium, and indium salts, are so conspicuous because they are compounds of three elements in the same family in the system, and thus exhibit the gradations required by the latter.

The chromic alums, the thallous alums, and the ammonium alums exhibit in each case the same peculiar relations to one another as do the alums of their kindred elements with normal behavior. In the case of the ammonium alums this is especially important, for it shows that whatever the determining cause of the properties of the alums may be, *exactly the same cause must be ascribed to the behavior of the ammonium salts as to that of the alums containing only metals:* since the ammonium radical has no true atomic weight, therefore the atomic weight itself is not the determining cause in the case of any alums whatsoever.

It is an interesting fact that the molecular volumes of the alums, when arranged according to their ascending values,

* The effect of this element upon its alums is shown by their melting-points, as will be described later.

bring both the trivalent and univalent elements into the same order as do their solubilities. In the following tables * the molecular volumes are given as calculated from Soret's determinations, with the double formulas, M_2SO_4, $M_2(SO_4)_3 . 24H_2O$ as the basis of the molecular weights. The solubilities are expressed in gram-molecules per liter.

	M^{III} = Al.		M^{III} = Cr.		M^{III} = Fe.	
	Mol. vol.	Solubility.	Mol. vol.	Solubility.	Mol. vol.	Solubility.
M^I = K	546.9	0.28	550.8	0.441	. . .	. . .
NH_4	555.9	0.387	557.6	0.407	562.8	1.659
Tl	566.6	0.177	557.7	0.234	560.2	0.799
Rb	562.2	0.059	561.7	0.079	573.3	0.376
Cs	579.2	0.013	581.8	0.015	579.3	0.045

	M^I = Cs.		M^I = (NH_4).	
	Mol. vol.	Solubility.	Mol. vol.	Solubility.
M^{III} = Al	578	0.013	555.9	0.387
Cr	582	0.015	557.6	0.407
Fe	579	0.045	562.8	1.659
In	584	0.172	. . .	. . .

The coincidence, while not absolute, shows that there is a close connection between the molecular volumes of the alums and their solubility. The variations, furthermore, lose much in weight in the fact that a very small error in the determination of the specific gravity is greatly multiplied in the quotient

$$\frac{\text{molecular weight}}{\text{specific gravity}}.$$

Solubility at Different Temperatures. — The next question to be decided was whether there is any regularity in the effect of increasing temperature upon the solubility of different alums. Here I was much limited in my choice of salts, insomuch as the ferric compounds break down into basic salts when treated with pure water at higher temperatures,

* Soret, Arch. sc. phys. nat. Genève, xii, 553, etc. Arzruni, Physikalische Chemie der Krystalle (1893), p. 130. Soret's original article is not at my disposal.

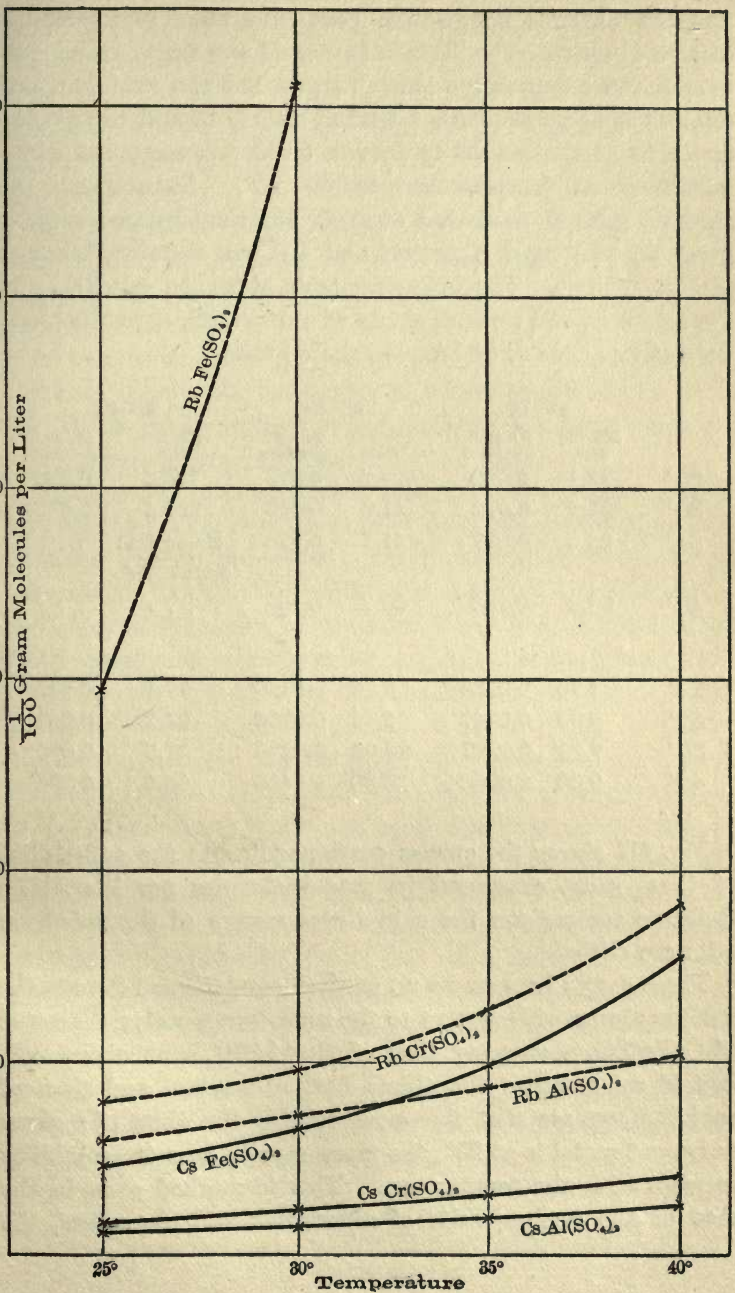

60
50
40
30
20
10
1/100 Gram Molecules per Liter
Rb Fe(SO4)2
Rb Cr(SO4)2
Rb Al(SO4)2
Cs Fe(SO4)2
Cs Cr(SO4)2
Cs Al(SO4)2
25°
30°
35°
40°
Temperature

FIGURE III.

and the chromic compounds pass into their green modifications at about 50°. This behavior of the ferric alums prevented the comparative study of any but the rubidium and cæsium compounds. As I wished merely to find the general direction of the solubility curves, I did not carry out determinations at temperatures below 25°. Experiments on chromic salts showed that even at 45° they became slightly green on prolonged digestion, and 40° was therefore taken as the upper limit. The following table gives the solubilities of the rubidium and cæsium alums of aluminium, chromium, and iron, at intervals of 5° between these limits.

	Rb—Al.		Rb—Cr.		Rb—Fe.	
	Pts. per liter.	Gr. mol. per liter.	Pts. per liter.	Gr. mol. per liter.	Pts. per liter.	Gr. mol. per liter.
25°	18.1	0.059	25.7	0.078	125.4	0.294
30°	21.9	0.072	31.7	0.096	202.4	0.617
35°	26.6	0.087	41.1	0.128	Basic salt separated.	. . .
40°	32.2	0.106	59.7	0.181	. . .	. . .
	Cs—Al.		Cs—Cr.		Cs—Fe.	
25°	4.70	0.0130	5.70	0.0150	17.1	0.045
30°	5.89	0.0167	9.60	0.0250	25.2	0.066
35°	7.29	0.0207	12.06	0.0320	37.5	0.099
40°	9.00	0.0256	15.30	0.0405	60.4	0.156

Fig. III shows the curves corresponding to the solubilities of these salts, expressed in gram-molecules per liter. To facilitate comparison the solubilities curves of the rubidium salts are dotted.

There seems here to be no marked connection between the various alums with respect to the univalent metals; the curve of $CsFe(SO_4)_2$ crossing that of $RbAl(SO_4)_2$ at about 33°. But if we compare the alums first of cæsium and then of rubidium, we see that the more soluble the alum of a given univalent metal is at 25°, the more rapidly does its solubility increase with the temperature. This is marked even in the case of the cæsium salts of aluminium and chromium, the

solubilities of which at 25° are almost the same (0.013 and 0.015 gr. mol.) The curve of $RbFe(SO_4)_2$ could be followed only to 30°, as at 35° a sparingly soluble basic salt separated from the solution; and the extreme difference in solubility shown for the interval 25°–30°, may in part be ascribed to a hydrolytic action.

Melting-points. — The melting-point of a hydrated salt is of course intimately connected with its solubility; so that in studying them one would expect results approximately analogous to the above. But at the same time I was enabled in this way to examine a greater variety of alums, including those of cobalt, the solubility of which could not be determined, the rubidium indium salt, and the potassium-vanadium and potassium-ferric compounds.

The cobaltic salts examined were those containing rubidium and cæsium. These were made in the same way as Marshall * obtained the ammonium and potassium cobaltic alums, by the electrolytic oxidation of cobaltous sulphate and addition of the calculated amount of the salt of the desired alkali metal. Both compounds came down in coarse crystalline grains, which could be readily washed by lixiviation with cold water. They were sufficiently stable to permit of rapid drying in the air, but on standing for any length of time they lost oxygen and yielded cobaltous sulphate. The rubidium alum decomposed in this matter even in a sealed specimen tube, on standing for a few months. The cæsium compound, however, when preserved in the same way, has still retained its green color; thus forming an interesting example of the greater stability of cæsium double salts over those of rubidium. Both compounds crystallized in glistening microscopic octahedrons. In view of their marked physical properties, it was not deemed necessary to submit them to a full analysis, but as a matter of general precaution a weighed quantity of each was ignited below a red heat, and the amount of the residual cobaltous and alkali-sulphates determined.

* Soc. Edinburgh, lix, 760.

0.0683 g. $RbCo(SO_4)_2.12H_2O$ gave 0.0361 g. $Rb_2SO_4 + CoSO_4$ calculated 0.0357 g.

0.7004 g. $CsCo(SO_4)_2.12H_2O$ gave 0.2962 g. $Cs_2SO_4 + CoSO_4$ calculated 0.2959 g.

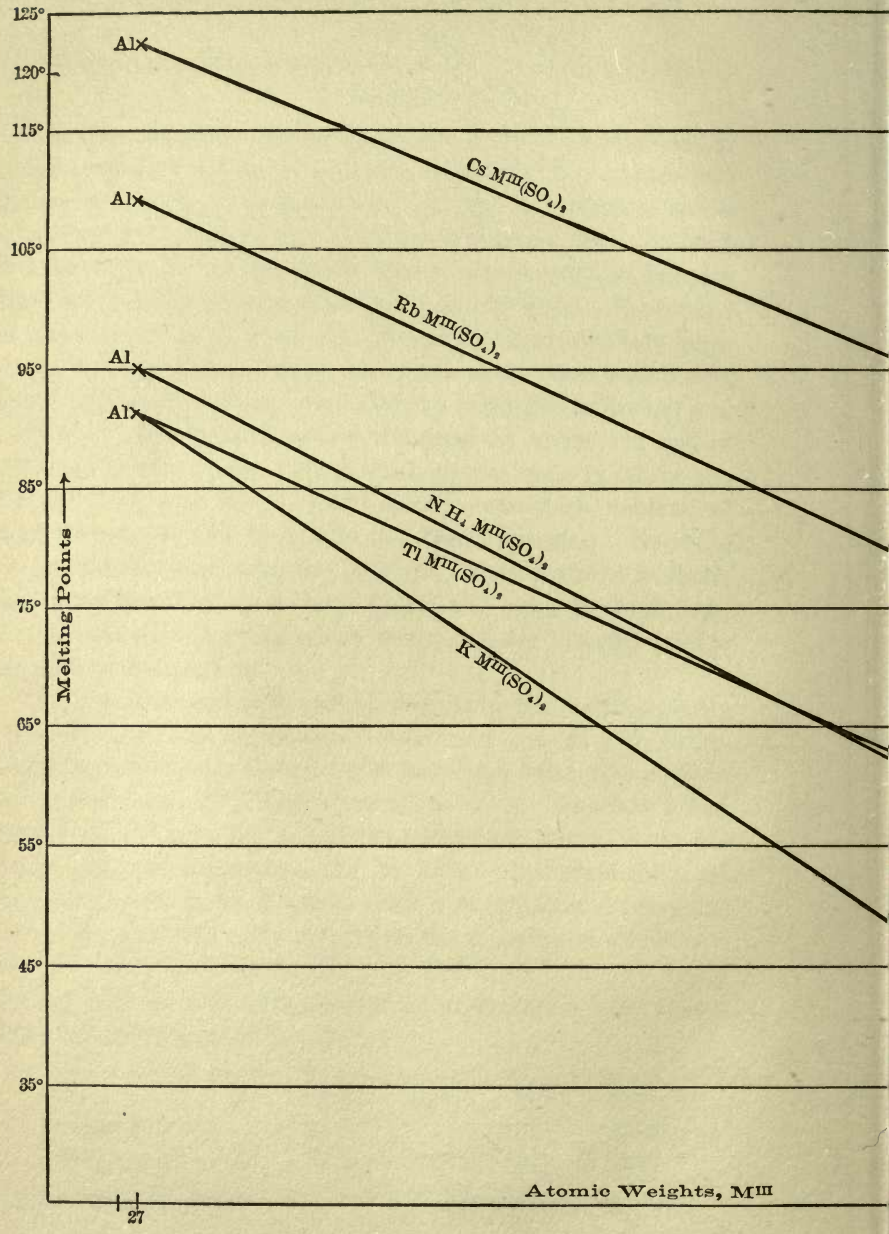
The determination of the melting-points was carried out in sealed capillary tubes, of various diameters, and about two inches in length. The tubes were in each case filled to somewhat over half their height with the powdered salts. At least five determinations were made on each compound, and samples from several different preparations used for each. Variations in the manner of heating, etc., introduce comparatively large errors in the melting-points, which are in no case very sharp. But after some practice, I was able, by carefully following one method of procedure, to reduce the error to about 1°; and in cases where two alums melted at about the same point, as the NH_4Al (95°) and NH_4Cr (94°) salts, comparative determinations were made side by side in the same apparatus. So while no pretence to great accuracy in these determinations is made, the errors involved are at least about the same for each compound, and thus the data given below are not vitiated for the purpose of comparison.

The literature contains various notices on the melting-points of aluminium- and chromium alums, and Piccini also determined approximately those of the vanadium salts with sodium (9°), potassium (20°), and ammonium (50°). The last I find to melt at 45°, and for vanadium potassium alum I have obtained data anywhere from 20° to 28°. The purification of this compound is so difficult that a constant melting-point cannot be observed. My results on the aluminium alums correspond fairly well with those of Erdmann,* though being slightly higher; and both his and mine are much higher than those determined by Tilden.†

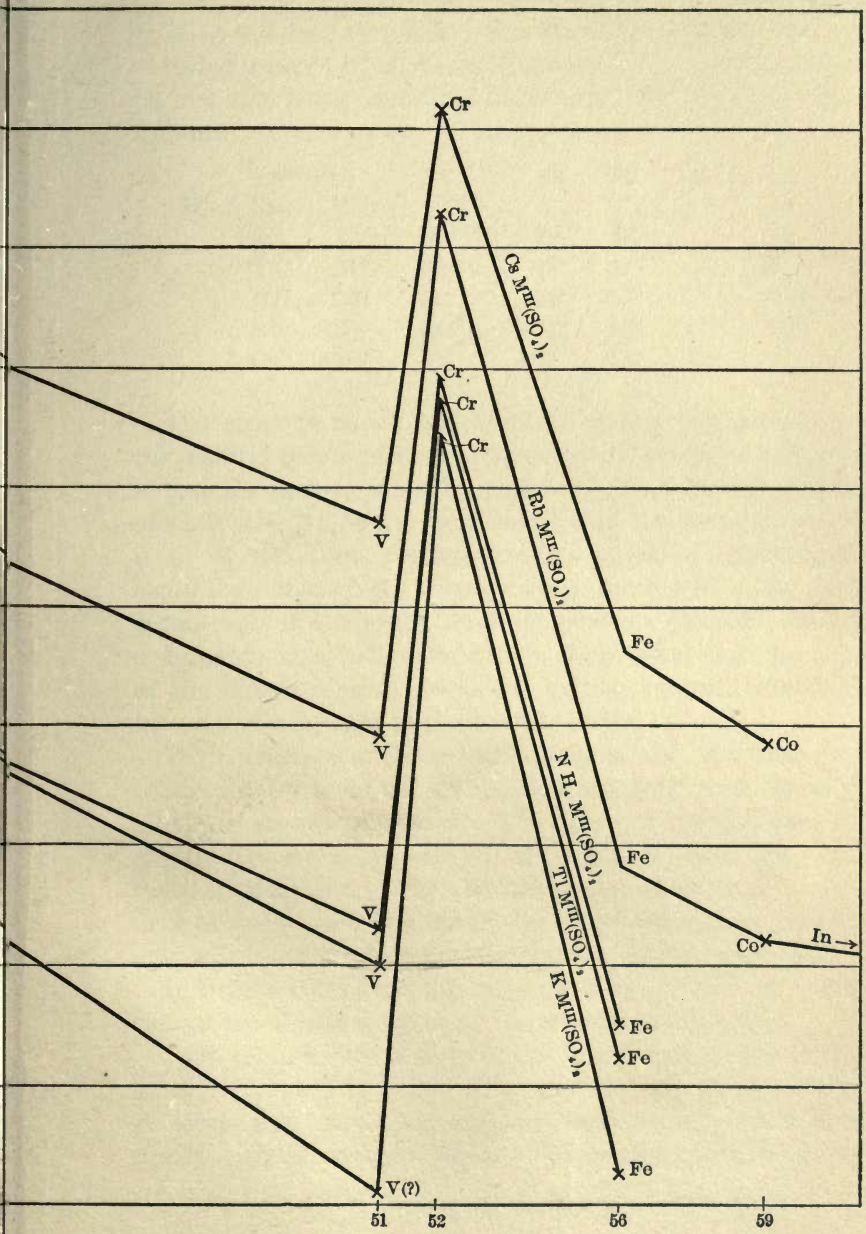
	Na—Al;	K—Al;	NH_4—Al;	Rb—Al;	Cs—Al.
Tilden . . .	61	84.5°	92°	99°	106°
Erdmann . . .		92.5°	. .	105°	120.5°
Locke . . .	63	91°	95°	109°	122°

* An. Pharm., ccxxxii, 3.

† London Soc. Trans., xlv, 266.


125°
120°
115°
105°
95°
85°
75°
65°
55°
45°
35°
Al
Al
Al
Al
Cs $M^{III}(SO_4)_2$
Rb $M^{III}(SO_4)_2$
NH_4 $M^{III}(SO_4)_2$
Tl $M^{III}(SO_4)_2$
K $M^{III}(SO_4)_2$
Melting Points
27
Atomic Weights, M^{III}

Fig


Cr
Cr
Cs Mn(SO4)2
Cr
Cr
Cr
V
Rb Mn(SO4)2
Fe
V
Co
N H4 Mn(SO4)2
Fe
Tl Mn(SO4)2
V
Co
In
V
K Mn(SO4)2
Fe
Fe
Fe
V(?)
51
52
56
59

E IV.

Observations on sodium-chromium and cæsium-indium alums gave no satisfactory results; the fusion process in each case covering a range of about ten degrees, and in the case of the indium salt, being even then imperfect. My complete results follow:

	M^{III} = Al.	V.	Cr.	Fe.	Co.	In.
M^{I} = Na	63°	(9°)*	. . .	. .	. .	. . .
K	91°	(20°)*	89°	28°	. .	. . .
Tl	91°	48°	92°	37°	. .	. . .
NH_4	95°	45°	94°	40°	. .	(36°)†
Rb	109°	64°	107°	53°	47°	42°
Cs	122°	82°	116°	71°	63°	. . .

The order in which the trivalent metals fall, according to the melting points of their alums with a given univalent metal, is here the same as when determined by the solubility relations of their salts. The one exception lies in the doubtful melting point of vanadium potassium alum, which is a few degrees lower than that of the corresponding ferric salt. The cobalt alums melt at a slightly lower temperature than do the iron compounds, and indium rubidium alum lower than any other of the rubidium salts, just as the indium cæsium alum is the most soluble member of the cæsium series.

With reference to the univalent metals also, the same graduation obtains as in the solubilities, but only in so far as the alkali metals are concerned. The order of the thallium and ammonium series is changed, the thallium salts lying next those of potassium. The vanadium compounds here form the only exception, and in view of their great instability it is to be doubted whether this is not due to unavoidable impurities.

In Figure IV, I give the melting-points plotted as a function of the atomic weights of the trivalent metals, R^{III}.

Here again we see a sharp break in the case of the chromic salts. The melting points of the cæsium and rubidium alums of aluminium, vanadium, iron, and cobalt are represented by nearly parallel *straight lines*, which would indicate a very

* Piccini, l. c.

† J. Prakt. Chemie (2), vii, 14.

simple relation between them, and the atomic weights of these metals. But we must either admit that the values of the melting-points are not dependable upon the atomic weights, or that the chromic alums form an exception to a law of nature.

III. The Solubilities of Alums as a Function of Two Variables.*

In my second paper in this series † I attempted to show that a definite gradation can be traced in the solubility of the alums of aluminium, vanadium, chromium, and iron, severally, with ammonium, thallium, rubidium, and cæsium. When the solubilities at 25° of the sixteen compounds considered, expressed in gram-molecules per liter of water, are plotted as a function of the atomic weights of the trivalent metals, a figure of remarkable regularity is obtained. The solubilities of the alums of aluminium, vanadium, and iron, with any given alkali metal, increase with the atomic weights of the trivalent metals; and this increase becomes the more pronounced as we pass from the caesium alums, through those of rubidium and thallium, to the ammonium salts, successively. But the alums of chromium, which stands between vanadium and iron in its atomic weight, are much less soluble than those of either of the latter metals. The sharp break in the curves, caused by this behavior of the chromium salts, indicates that although the method of plotting employed illustrates the general gradation of the solubilities, the latter cannot truly be regarded as a function of the atomic weights. The solubilities, as determined, are as follows:

	M^{III} = Al.	V.	Cr.	Fe.
M^{I} = Cs	0.013	0.0204	0.0151	0.045
Rb	0.059	0.177	0.078	0.293
Tl	0.177	0.573	0.212	0.799
NH_4	0.387	1.210	0.407	1.659

* Amer. Chem. Jour., xxvi, August, 1901. † See the preceding article.

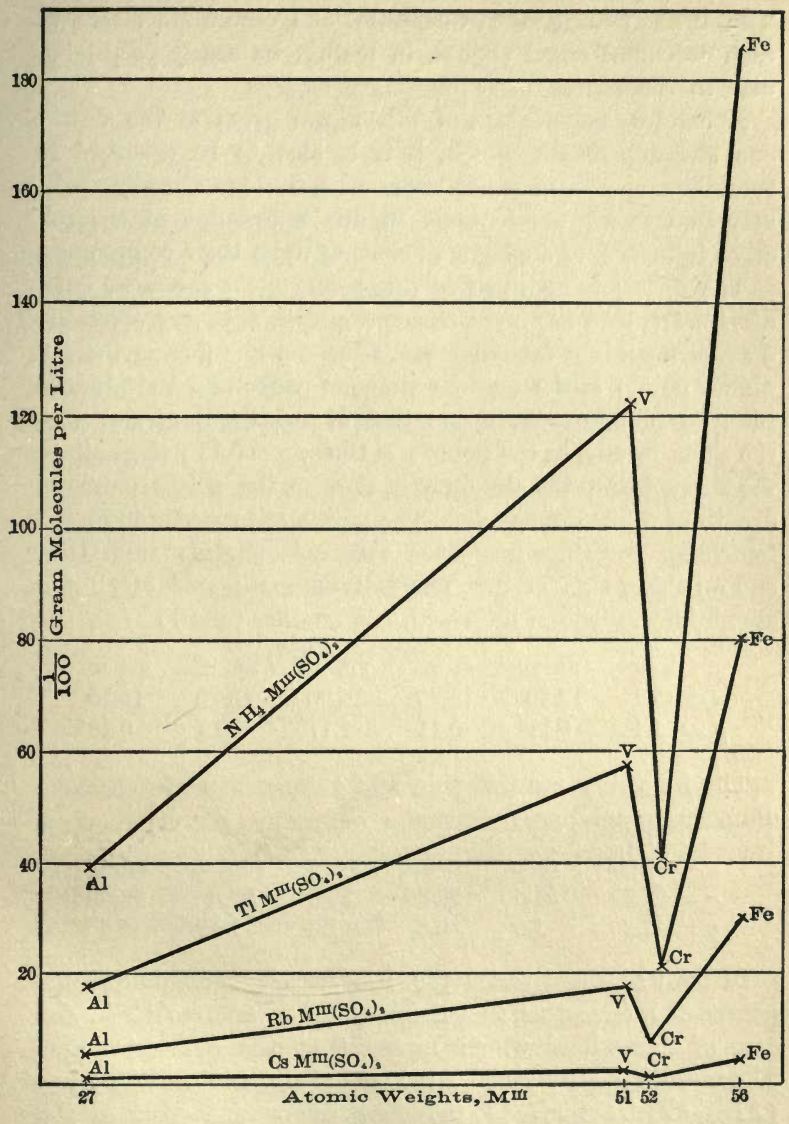


FIGURE I.

Fig. 1 reproduces these relations. For the sake of clearness, the values are slightly increased along the x-axis.

The lines joining the vanadium and chromium alums of each univalent metal should, in reality, be nearly perpendicular to the x-axis.

A careful examination of this figure gives at the outset one striking result, which, if it is also to be observed in solubility charts of other series of homologous compounds, may lead to a great advance in our knowledge of the relative influence of analogous elements upon their compounds.

The lines joining the *solubility points of the successive univalent metals with two given trivalent metals, have approximately a common point of intersection.* Thus, the line joining the solubility points of the cæsium alums of vanadium and aluminium, on prolongation, meets that of the thallium alums of the same metals, in the point $x = 16.25$, $y = 0.11$; the unit on the x-axis being the atomic unit, that on the y-axis one-hundredth of a gram-molecule. The points of intersection of the remaining corresponding lines vary only slightly from this, and on either side of it. The intersection points of all the aluminium-vanadium lines with one another follow:

	Cs—Rb.	Rb—Tl.	Cs—Tl.	NH_4—Cs.	NH_4—Rb.	NH_4—Tl.
$x =$	18.1	16.30	16.25	16.00	15.70	15.10
$y =$	1.1	0.11	0.11	1.17	0.15	0.12

The following are the points of intersection of the vanadium-chromium lines:

	Rb—Cs.	Tl—Cs.	Tl—Rb.	NH_4—Cs.	NH_4—Rb.	NH_4—Tl.
$x =$	52.99	52.6	52.65	52.6	52.6	52.53
$y =$	1.2	1.3	0.8	1.4	1.45	5.3

In both of these series the nearest approximation of the points of intersection to a single point is seen to be in the case of those lines which intersect at the greatest angle. The most marked variations are that of the (AlCs—VCs) and (AlRb—VRb) lines in the first series, and that of the (VTl—CrTl) and (VNH_4—$CrNH_4$) lines in the second; that is, where the lines in question are most nearly parallel, and where, therefore, unavoidable error of experiment would pro-

duce the greatest divergence. The various other lines, such as those of (FeM^I–CrM^I), (FeM^I–AlM^I), or (CrM^I–AlM^I), show a similar relation as regards their points of intersection, and it must be assumed, therefore, that the points representing the *solubilities stand in fixed mathematical relation to one another.*

This being so, the derivation of a general formula for the calculation of the solubility of the sixteen alums in question is a comparatively simple matter. The first step involved is the empirical determination of the fixed points, of which the observed points of intersection are approximations. Of these, the three giving respectively the intersections of the lines (VM^I–AlM^I), (VM^I–CrM^I) and (CrM^I–FeM^I) are required.

The points finally selected as most nearly satisfying all the solubilities are as follows:

$$\text{For } (VM^I - AlM^I) \quad \begin{cases} x = 16.1 \\ y = 0.8 \end{cases}$$

$$\text{“ } (VM^I - CrM^I) \quad \begin{cases} x = 52.61 \\ y = 1.5 \end{cases}$$

$$\text{“ } (CrM^I - FeM^I) \quad \begin{cases} x = 50.81 \\ y = 0.6 \end{cases}$$

Radii drawn from these points gave by intersection with perpendiculars raised on the x-axis at points corresponding to the atomic weights of the trivalent metals, the following solubilities in gram-molecules. Under D is given the variation from the observed solubilities.

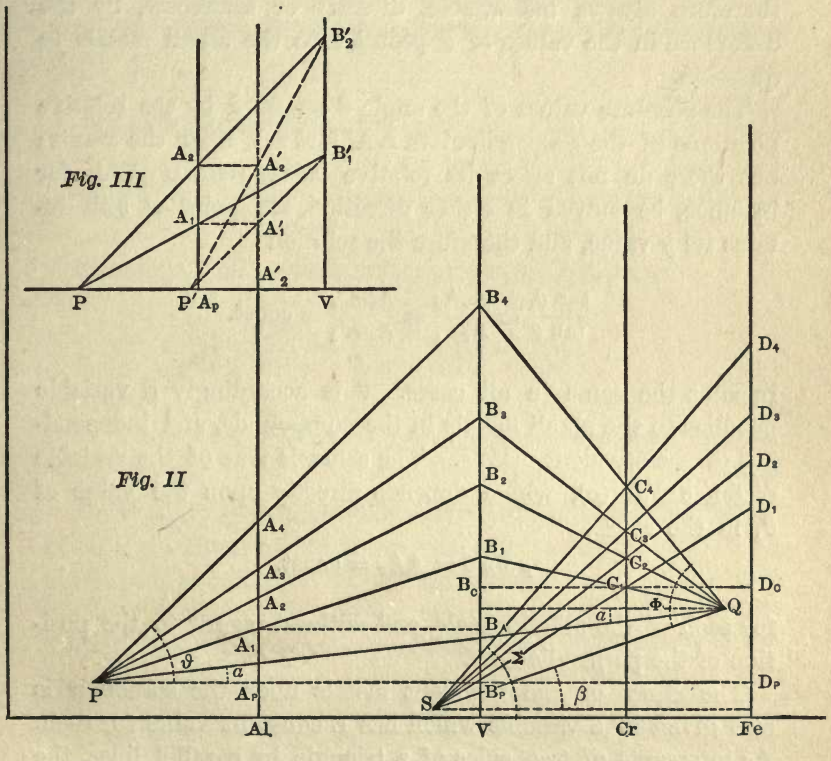
	M^{III}=Al	D.	V.	D.	Cr.	D.	Fe.	D.
M^I=Cs	0.012	–0.001	0.0209	+0.0005	0.0169	+0.0018	0.0498	+0.0048
Rb	0.064	+0.005	0.1878	+0.0108	0.0734	–0.0046	0.2776	–0.0169
Tl	0.182	+0.005	0.5670	–0.0060	0.2014	–0.0106	0.7922	–0.0068
NH_4	0.382	–0.006	1.2090	–0.0010	0.4182	+0.0112	1.6643	+0.0016
Average errror,		+0.001		+0.001		–0.0005		–0.0043

As is seen, the agreement between the observed and calculated data is in the main very satisfactory. In more than half the cases the difference does not exceed 0.005 gram-molecule. The average molecular weight of an alum is about 300, and the error represented by a difference of 0.001 gram-molecule therefore means about 0.3 g. per liter. As the majority of my determinations were made with quantities of solutions containing about 3.0 g. of water, therefore, an error of this magnitude would represent on the average less than a milligram in weight; or in the case of the ammonium alums, where the dissolved salts were determined as sesquioxides, less than 0.5 milligram. A very slight variation in temperature, in the case of the more soluble alums, introduces a still greater error. At 30°, one liter of water dissolves 0.467 gram-molecule ammonium aluminium alum, and 0.495 gram-molecule ammonium chromium alum. The increase in solubility for 5° is therefore in the one case 0.080, in the other 0.088 gram-molecule. Assuming that for so short an interval the solubility is directly proportional to the temperature, a variation of 0.2° would cause an error of more than 0.003 gram-molecule. The range of solubility of the alums is so great that errors of such magnitude would have little influence upon the determination of the general solubility relations of the salts; and such relations were all that I had hoped to establish by the work embodied in my last paper. If we take into account the effect which the more or less extensive hydrolytic dissociation of the sulphates of the trivalent metals would have upon the solubility of the alums,* the variation between the solubilities, calculated and observed, is in almost every case well within the limit of permissible error. In the derivation of the constants used in this paper, therefore, the calculated results will be taken as correct.

The prolongation of the aluminium-vanadium lines and of the vanadium-chromium lines to their respective points of intersection yields a series of triangles which have a common

* This of course also applies to the formation of small quantities of basic salts on evaporation of the solutions for analysis.

base in the line connecting these points. A similar set of triangles is given by the intersection of the vanadium-chromium lines with those of chromium-iron. The resulting figure, somewhat distorted in its proportions, is shown in Fig. II.



The perpendiculars, AAl, BV, CCr, and DFe, and the fixed points, P, Q, and S being given, the points of intersection of the radii from P, Q, and S with the perpendiculars BV, CCr, and DFe, are necessarily determined by the position of the points of intersection of the corresponding radii from P with the perpendicular AAl. Now the points A_1, B_1, C_1, and D_1 represent the solubilities of the cæsium alums of the successive trivalent metals; A_2, B_2, C_2, and D_2, those of the rubidium alums, etc. The line A_1P makes a definite angle, θ,

with the x-axis, and the points B_1, C_1, D_1, are accordingly determined by the value of this angle. If we substitute rubidium for cæsium, θ receives another value and B, C, and D become B_2, C_2, D_2. The effect of the substitution of any one alkali metal for another in the alums of a trivalent metal is therefore always measurable, directly or indirectly, by the difference in the values of θ peculiar to the alkali metals in question.

The absolute values of the angle θ are fixed by the relative positions of the perpendiculars AAl and BV upon the x-axis; but these do not affect its relative values; for if AAl, for instance, be moved in either direction, the point P still retains its y value, and therefore the relation

$$\frac{\tan\theta_1}{\tan\theta} = \frac{A_PA_2}{A_PA_1} = \frac{A_{P'}A'_2}{A_{P'}A'_1} = \text{const.}$$

remains the same in all cases. θ is accordingly a variable peculiar to the alkali metals in the compounds, and independent of the trivalent metals. The same is true of the variable distance PA (ρ), which depends directly upon the value of θ, in the sense,

$$\rho \sin\theta = AA_P = \text{const.}$$

for each of the alkali metals, and without regard to the position of the perpendiculars.

The effect of the trivalent metals upon the solubility is also given by a variable which has a constant value for each. As intercepts of two sides of a triangle by parallel lines, the relations obtain:

$$\frac{A_1B_1}{A_1P} = \frac{A_2B_2}{A_2P} = \frac{A_3B_3}{A_3P} = \ldots = k$$

$$\frac{B_1C_1}{C_1Q} = \frac{B_2C_2}{C_2Q} = \ldots = k_1$$

$$\frac{C_1D_1}{SC_1} = \frac{C_2D_2}{SC_2} = \ldots = k_2$$

These constants, k, k_1, and k_2, are independent of the value of the angle θ, and therefore of the univalent metals in the alums. They are also independent of the positions of the perpendiculars AAl, etc. If the relative positions of AAl and BV be altered, for instance, until P becomes P′ (Fig. III), the ratio between the new intercepts, $\frac{A_1'B_1'}{A_1'P'}$, is still the same as $\frac{A_1B_1}{A_1P}$, or k.

We have, furthermore, the relation,

$$\frac{B_1B_2}{A_1A_2} = \frac{B_2B_3}{A_2A_3} = \ldots = \frac{PA + AB}{PA} = \frac{\rho(k+1)}{\rho} = k + 1$$

Similarly, for the vanadium and chromium alums,

$$\frac{C_1C_2}{B_1B_2} = \frac{C_2C_3}{B_2B_3} = \frac{C_1Q}{C_1Q + k_1CQ} = \frac{1}{k_1 + 1}$$

$$\frac{D_1D_2}{C_1C_2} = \frac{D_2D_3}{C_2C_3} = \ldots = \frac{SC + k_2SC}{SC} = k_2 + 1$$

Now A_1A_2 represents the difference in solubility of the aluminium alums of rubidium and cæsium; C_1C_2, that of the chromium alums, etc. If we call the difference in the solubility of the alums of a given trivalent metal with two alkali metals the "increment of solubility for the latter" (e. g., $\text{Incr.Al}_{\text{Rb-Cs}}$), we arrive at the general law:

The ratio between the increments of solubility of the corresponding alums of two trivalent metals for any two alkali metals is constant.

The constant k indirectly represents, therefore, the effect of the substitution of vanadium for aluminium in the alum of a given univalent metal; k_1, that of chromium for vanadium, etc. And since the value of these constants is not affected by the relative positions of the perpendiculars upon the x-axis, the atomic weights of the trivalent metals have no determining influence upon them. The solubilities cannot, therefore, be regarded as a function of these atomic weights.

The values of the constants k, etc., for the calculated solubilities are as follows:

$$k = 2.2110$$
$$k_1 = 1.9608$$
$$k_2 = 3.0213$$

By substitution, we have, furthermore, for the ratio between the solubility increments of the alums of other pairs of trivalent metals,

$$\frac{C_1C_2}{A_1A_2} = \frac{\text{Incr.Cr}_{m^2-m'}}{\text{Incr.Al}_{m^2-m'}} = \frac{k+1}{k_1+1} = 1.0844$$

$$\frac{D_1D_2}{A_1A_2} = \frac{\text{Incr.Fe}_{m^2-m'}}{\text{Incr.Al}_{m^2-m'}} = \frac{k+1}{k_1+1}(k_2+1) = 4.3604$$

$$\frac{D_1D_2}{B_1B_2} = \frac{\text{Incr.Fe}_{m^2-m'}}{\text{Incr.V}_{m^2-m'}} = \frac{k_2+1}{k_1+1} = 1.3580$$

Owing to the large error introduced into the quotient of the observed solubility increments by variations of a few thousandths of a gram-molecule in the solubility determinations, we can expect only an approximate agreement between the above constants and their observed values. The latter, which, together with the variations from the calculated values (D), are given below, are therefore eminently satisfactory. The agreement between them is so marked that there can be no doubt as to the correctness of the law.

$$\frac{\text{Incr.Al}_{m^2-m'}}{\text{Incr.V}_{m^2-m'}} = 3.211 \qquad \frac{\text{Incr.Cr}_{m^2-m'}}{\text{Incr.V}_{m^2-m'}} = 0.3377$$

m^2.	m'.	Observed.	D.	Observed.	D.
NH_4	Cs	3.181	—0.030	0.3295	—0.0085
Tl	Cs	3.378	+0.167	0.3561	+0.0184
Rb	Cs	3.404	+0.190	0.4016	+0.0693
NH_4	Rb	3.149	—0.074	0.3185	—0.0192
Tl	Rb	3.356	+0.145	0.3384	+0.0007
NH_4	Tl	3.033	—0.178	0.3197	—0.0316

$\frac{\text{Incr.Fe}_{m^2-m'}}{\text{Incr.Cr}_{m^2-m'}} = 4.021$ $\qquad$ $\frac{\text{Incr.Cr}_{m^2-m'}}{\text{Incr.Al}_{m^2-m'}} = 1.084$

m^2.	m'.	Observed.	D.	Observed.	D.
NH_4	Cs	4.118	+0.097	1.021	−0.063
Tl	Cs	3.829	−0.192	1.200	+0.116
Rb	Cs	3.957	−0.064	1.152	+0.068
NH_4	Rb	4.119	+0.098	1.003	−0.081
Tl	Rb	3.770	−0.250	1.127	+0.043
NH_4	Tl	4.410	+0.389	0.927	−0.159

$\frac{\text{Incr.Fe}_{m^2-m'}}{\text{Incr.Al}_{m^2-m'}} = 4.360$ $\qquad$ $\frac{\text{Incr.Fe}_{m^2-m'}}{\text{Incr.V}_{m^2-m'}} = 1.358$

m^2.	m'.	Observed.	D.	Observed.	D.
NH_4	Cs	4.316	−0.044	1.357	−0.001
Tl	Cs	4.537	+0.177	1.363	+0.005
Rb	Cs	5.411	+1.051	1.606	+0.186
NH_4	Rb	4.164	−0.196	1.322	−0.031
Tl	Rb	4.200	−0.080	1.276	−0.067
NH_4	Tl	4.095	−0.265	1.350	−0.008

The only marked deviations from the calculated constants are in the case of $\frac{\text{Incr.Cr}_{Rb-Cs}}{\text{Incr.V}_{Rb-Cs}}$, where both increments are so small that even the slightest error of experiment has a great influence upon their ratio; and in some of the ratios obtained with rubidium ferric alum. The observed solubility of this salt is probably somewhat high, owing to the readiness with which it undergoes hydrolysis. The error thus introduced, however, becomes very great only in the ratios $\frac{\text{Incr.Fe}_{Rb-Cs}}{\text{Incr.M}^{II}_{Rb-Cs}}$. In the ratios $\frac{\text{Incr.Fe}_{NH_4-Rb}}{\text{Incr.M}^{III}_{NH_4-Rb}}$ its influence is hardly felt.

The remaining variables of the triangles PBQ and SCQ, so far as their values are necessary for the derivation of a general formula for the solubilities, are also to be expressed in terms of θ, and k, k_1, etc.

If we call the angle of inclination of the base line PQ to the x-axis, a, then for the variable angle, BQP, or ϕ, we have the expression:

$$\tan \phi = \frac{\text{PB} \sin (\theta - a)}{\text{PQ} - \text{PB} \cos (\theta - a)} = \frac{\rho (k+1) \sin (\theta - a)}{\text{PQ} - \rho (k+1) \cos (\theta - a)}.$$

In this formula, a and PQ are constant. Substituting for the latter and k their calculated values, we have,

$$\tan \phi = \frac{\rho \sin (\theta - a)}{11.37 - \rho \cos (\theta - a)} = R.$$

Since $$\text{B}_1\text{Q} = \frac{\text{B}_1\text{P} \sin (\theta - a)}{\sin \phi},$$

the variable distance BQ becomes

$$\text{BQ} = \frac{\rho (k+1) \sin (\theta - a)}{\frac{\tan \phi}{\sqrt{1 + \tan^2 \phi}}}$$

$$= \frac{\rho (k+1) \sin (\theta - a) \sqrt{1 + R^2}}{R} = M.$$

As the intercepts $\text{BC} = k_1 \text{CQ}$ and, therefore,

$$\text{M} = \text{BC} + \frac{\text{BC}}{k_1},$$

the relation which these intercepts bear to M are

$$\text{BC} = \frac{k_1 M}{k_1 + 1} \text{ and } \text{CQ} = \frac{M}{k_1 + 1}.$$

The base line SQ makes with the x-axis the constant angle β; the variable angle BQS is therefore $\phi + \beta - a$. For the angle DSQ, or Σ, we have, as in the case of the angle ϕ,

$$\tan \Sigma = \frac{\text{CQ} \sin (\phi + \beta - a)}{\text{SQ} - \text{CQ} \cos (\phi + \beta - a)}.$$

The value of a is 1° 5′ 54″, and that of β, 26° 33′ 54″. Ex-

panding, and substituting for these and SQ their corresponding values, and for CQ its equivalent, $\frac{M}{k_1 + 1} = \frac{M}{2.9608}$, we have

$$\tan \Sigma = \frac{M(R + 0.4763)}{6.401\sqrt{1 + R^2} - M(1 - 0.4763\,R)}.$$

The distance $AA_P = \rho \sin \theta$. The solubility of the aluminium alums is therefore expressed by the equation,

$$S_{Al} = m + \rho \sin \theta \qquad (1)$$

m being the y-value of the point P. For the solubility of the vanadium alums we have,

$$BB_p = BB_A + AA_P, \qquad (2)$$

and since $BB_A = k\rho \sin \theta$,
by addition with (1),

$$S_V = m + \rho \sin \theta + k\rho \sin \theta.$$

Passing in the same manner to the chromium alums,

$$CC_p = BB_p - BB_c$$

$$= BB_p - \frac{k_1 M}{k_1 + 1} \sin (\phi - \alpha),$$

and, accordingly,

$$S_{Cr} = m + \rho \sin \theta + k\rho \sin \theta - \frac{k_1 M}{k_1 + 1} \sin (\phi - \alpha). \qquad (3)$$

The points D_1, D_2, etc., are expressed by

$$S_{Fe} = m + DD_p$$

$$= m + DD_c + CC_p$$

in which $DD_c = CD \sin (\Sigma + \beta)$.

The variable distance CD is given by the equation,

$$CD = k_2\,CS$$

$$= \frac{k_2\,CQ \sin (\phi + \beta - \alpha)}{\sin \Sigma}$$

$$= \frac{k_2 M \sin(\phi + \beta - \alpha)}{(k_1 + 1) \sin \Sigma}$$

Substituting this value for CD, we have

$$S_{Fe} = m + CC_p + \frac{k_2 M \sin(\phi + \beta - \alpha)}{(k_1 + 1) \sin \Sigma} \sin(\Sigma + \beta)$$

or

$$S_{Fe} = m + \rho \sin\theta + k\rho \sin\theta - \frac{k_1 M}{k_1 + 1} \sin(\phi - \alpha) + \frac{k_2 M \sin(\phi + \beta - \alpha)}{(k_1 + 1) \sin \Sigma} \sin(\Sigma + \beta).$$

This also serves as a general formula for the solubility (S) of any of the sixteen alums taken into consideration. For if k_2 be made equal to zero, the last term falls away, leaving the equation in the forms applying to the chromium alums. With k_2 and k_1, equal to zero, the solubilities of the vanadium alums are obtained, and by eliminating the second term as well, those of the aluminium salts. We thus have a general solubility equation, all the terms of which can be referred to two variables; the one of these, θ, applying to the one class of elements in the compounds, the other, k, to the second class. I believe that aside from the instance of addition properties, which the solubilities certainly are not, this is the first case in which a mathematical relation between the corresponding properties of a class of compounds has been found capable of expression.

Below I give the values of θ and ρ for each of the alkali metals, and the solubilities as calculated by the general formula. With the latter, the column D contains the difference between the calculated and observed solubilities, and D′ the variation from the values serving as a basis for the derivation of the constants.

	θ	ρ
Cs	2° 6′ 5″	10.945
Rb	27° 11′ 19″	12.254
Tl	57° 56′ 4″	20.5406
NH	73° 45′ 5″	38.943

In the following the solubilities are expressed in hundredths of a gram-molecule:

	Al.	D.	D′.	V $k_1 = 2.2110$.	D.	D′.	Cr $k_1 = 1.9608$.	D.	D′.	Fe $k_2 = 3.0213$.	D.	D′.
Cs	1.192	−0.0108	−0.008	2.06	+0.02	−0.03	1.671	+0.16	−0.02	4.82	+0.32	−0.16
Rb	6.38	+0.328	−0.020	18.90	+1.20	+0.12	7.34	−0.36	0.00	27.76	−1.63	+0.06
Tl	18.21	+0.510	+0.010	56.7	−0.60	0.00	20.13	−1.07	+0.01	79.69	−0.30	+0.47
NH_4	38.18	+0.520	−0.020	120.82	−0.08	−0.07	41.82	+1.12	0.00	165.26	−0.64	−1.17

In conclusion I may state that while the data now at hand are too few for accurate analysis, such determinations as I have made at temperatures other than 25° indicate that a general solubility formula for all temperatures will not be difficult of derivation. I have made determinations at 30° on the cæsium, rubidium, and ammonium alums of aluminium, chromium, and iron; and find that the law of the constant ratio of the solubility increments holds good at that temperature. The value of the constants k, k_1, and k_2, however, vary with the temperature. At 30°

$$\frac{\text{Incr.Cr}_{m^2-m'}}{\text{Incr.Al}_{m^2-m'}} = 1.20, \text{ and } \frac{\text{Incr.Fe}_{m^2-m'}}{\text{Incr.Cr}_{m^2-m'}} = 8.3$$

in approximate numbers. From the fact that this law obtains at other temperatures, it necessarily follows that at these, as at 25°, the lines joining the solubility points have common points of intersection. The same formula, therefore, with other constants, obtains at different temperatures. The mathematical relation between the solubilities at 25° cannot, accordingly, be a matter of chance.

My thanks are due to Eugene Lamb Richards, Professor of Mathematics in Yale University, for many helpful suggestions embodied in this paper.

PAPERS ON
DOUBLE HALOGEN SALTS

ON SOME DOUBLE HALIDES OF SILVER AND THE ALKALI METALS.*

By H. L. WELLS and H. L. WHEELER.

WITH THEIR CRYSTALLOGRAPHY.

By S. L. PENFIELD.

During a systematic search for well-crystallized salts of the type M'Hl.AgHl, † which we were anxious to obtain on account of their probable isomorphism with the alkaline trihalides, three well-defined compounds of another type, 2M'Hl.AgHl, were obtained. Our experience indicates that these 2 : 1 salts are more easily prepared and crystallize better than the 1 : 1 compounds.

The bodies to be described are 2CsCl.AgCl, 2RbI.AgI, and 2KI.AgI. Two of these are believed to be new salts; the other, 2KI.AgI has been described by Boullay.‡ We have not obtained a complete series of these compounds, for good crystals could not be made of the other members, and, under the circumstances, no products were analyzed except such as could be measured.

The compounds are interesting from the fact that they do not conform to Remsen's law concerning the composition of double halides, § for, contrary to this, they contain a number of alkali-metal atoms which is greater than the number of halogen atoms belonging to the silver. In his latest contribution to the subject, ‖ Remsen states that the exceptions to his law are "not more than three or four out of over four

* Amer. Jour. Sci., xliv, August, 1892.
† Ibid., III, xliii, 30 and 485.
‡ Ann. Chim. Phys., II, xxiv, 377.
§ Amer. Chem. Jour., xi, 291.
‖ Ibid., xiv, 87.

hundred." The work here described confirms the result of Boullay, adds two more exceptions to the law, and points to the existence of a greater number of compounds of the same type. It may be mentioned that a considerable number of other exceptions to this law have recently been established in this laboratory and will soon be described.

Preparation and Properties. — The salts are made by saturating a very concentrated, hot solution of an alkaline halide with the corresponding silver halide, filtering, cooling to crystallization, and, if necessary, evaporating the mother-liquor at ordinary temperatures. If the solutions are too dilute, in some cases at least, the 1 : 1 salts are formed. The compounds have little tendency to crystallize well, and many trials are usually necessary in order to obtain satisfactory products. The salts are all white. They are readily decomposed by water.

Method of Analysis. — The products analyzed were in the form of crystals of such size that it was certain that they were not mixed with other substances. In preparing them for analysis the mother-liquor was removed rapidly and completely by pressing them between smooth filter-papers, and great care was taken to avoid any evaporation of the liquid which adhered to them. The analyses were made by treating them with a sufficient amount of water acidified with nitric acid and weighing the silver halide thus separated. The filtrate from this was used for determining the remaining halogen or the alkali metal.

	Found.	Calculated for 2CsCl.AgCl.
Cæsium		55.38
Silver	24.85	22.47
Chlorine		22.15

	Found.	Calculated for 2RbI.AgI.
Rubidium . . .	25.05	25.91
Silver	17.32	16.36
Iodine	57.53	57.73
	99.90	100.00

	Found.	Calculated for 2KI.AgI.
Potassium		13.79
Silver	18.73	19.04
Iodine		67.17

Crystallography.

The three salts are isomorphous and crystallize in the orthorhombic system. The forms which were observed are:

a, 100, $i\text{-}\bar{i}$	*m*, 110, *I*	*d*, 101, $1\text{-}i$
b, 010, $i\text{-}\check{i}$	*n*, 120, $i\text{-}2$	*x*, 301, $3\text{-}\bar{i}$

The axial ratios and some of the prominent angles are given in the following tables, the fundamental measurements being marked by an asterisk. The crystals did not yield very accurate measurements.

	$\dot{a} : \bar{b} : \dot{c}$
2CsCl.AgCl	0.971 : 1 : 0.244
2RbI.AgI	0.977 : 1 : 0.236
2KI.AgI	0.977 : 1 : 0.234

	$m \wedge m$, 110 $\wedge$ 110	$n \wedge n$, 120 $\wedge \bar{1}20$	$d \wedge d$, 101 $\wedge \bar{1}01$
2CsCl.AgCl . .	88° 18′	*54° 29′	*28′ 11′
2RbI.AgI . . .	*88° 40′	54° 12′	*27′ 12′
2KI.AgI . . .	*88° 40′	54° 12′	*27′ 0′

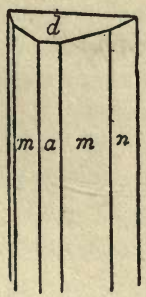


Fig. 1.

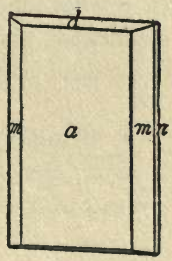


Fig. 2.

2CsCl.AgCl was made in minute prisms, less than a millimeter in diameter, having the habit shown in Fig. 1. The measurements are only approximately correct.

Two crops of 2RbI.AgI were examined. One was like Fig. 1 in habit, the other in plates, Fig. 2. The crystals were nearly 10 mm. in length. On this salt a cleavage, parallel to *a*, was observed; also, as small faces, the forms *b* and *x*, which are not shown in the figures. In convergent polarized light an obtuse bisectrix was seen, normal to *a*, the axial plane being the brachy-pinacoid.

2KI.AgI was made in prismatic crystals, over 10 mm. in length and having the habit and forms shown in Fig. 1.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1892.

ON THE CÆSIUM AND RUBIDIUM CHLORAURATES AND BROMAURATES.*

By H. L. WELLS and H. L. WHEELER.

WITH THEIR CRYSTALLOGRAPHY.

By S. L. PENFIELD.

A study of the compounds to be described was undertaken in the hope that some crystallographic analogy would exist between them and the alkaline pentahalides described in a previous article.† No such analogy has been found in spite of the similarity of such formulæ as $CsCl.Cl_3I$ and $CsCl.Cl_3Au$, but since some of these gold salts have never been described and as they show some interesting relations among themselves, our results are deemed worthy of publication.‡

Th. Rosenbladt,§ in an article on the solubility of the chloraurates, states that the cæsium and rubidium salts lose their water of crystallization almost completely when dried over sulphuric acid. He gives no statement of the amount of water, but refers to his dissertation of 1872, which is inaccessible to us. He mentions, however, that the crystals of both salts belong to the monoclinic system, so that it is probable that the compounds he obtained were the ones that we have found to be anhydrous.

The compounds that have been prepared are $CsAuCl_4$, $2CsAuCl_4.H_2O$, $CsAuBr_4$, $RbAuCl_4$, and $RbAuBr_4$. We have attempted in each case to obtain bodies containing more

* Amer. Jour. Sci., xliv, August, 1892.

† Ibid., 42.

‡ The announcement by Professor Remsen (Amer. Chem. Jour., xiv, 89), that he and Mr. H. C. Jones proposed to examine the gold-rubidium halides, was not made until after the work described in this article had been completed.

§ Berichte, xix, 2535.

cæsium and rubidium, but no evidence of their existence has been found.

An investigation of the corresponding iodine compounds was also undertaken, but, on account of the instability of auric iodide, we did not obtain any pure or well-crystallized products.

Preparation. — The salts are so insoluble that they form precipitates when moderately concentrated solutions of the component salts are mixed, and the products are readily recrystallized from water or from the mother-liquors. It is usually immaterial whether the solutions are neutral or acid or whether the gold or alkaline halide is in excess, but the salt $2CsAuCl_4.H_2O$ requires special conditions for its preparation, for it is apparently formed only when a large excess of gold chloride is present and when the solution does not contain much free acid. We have used four atoms of gold to one of cæsium in making this salt, but it usually requires repeated trials under these conditions before it is obtained free from the anhydrous compound. The two salts are however so distinct in form that there is no difficulty in distinguishing them.

Properties. — The color of $CsAuCl_4$ and of $2CsAuCl_4.H_2O$ is golden-yellow; $RbAuCl_4$ is yellowish-red; the two bromides are black, but give a dark red powder.

All the salts are sparingly soluble in water, especially when cold, and the cæsium compounds are less soluble than the rubidium. All of them are only slightly soluble in alcohol and insoluble in ether.

Methods of Analysis. — The crystals were prepared for analysis by quickly pressing them between smooth filter-papers and finally allowing them to become air-dry. The hydrous cæsium chloraurate, however, loses its water and becomes opaque on exposure. It was therefore dried as rapidly and thoroughly as possible on paper, and was put into a weighing-tube as soon as some of the fragments began to lose their transparency.

Gold was determined by precipitation with ammonium oxalate or with sulphurous acid. The filtrate from the metallic

gold was used either to determine the alkali metal as normal sulphate or the halogen by the usual gravimetric method. Water was determined by the method used in the combustion of organic compounds, the halogens being held back by a mixture of lead chromate and lead oxide. The absence of water in the anhydrous compounds was established by the use of the same process.

	Found.	Calculated for $CsAuCl_4$.
Cæsium . . .	28.11	28.16
Gold	41.61	41.77
Chlorine . .	29.91	30.06
	99.63	

	Found.			Calculated for $2CsAuCl_4.H_2O$.
Cæsium . . .	27.23	. . .	. . .	27.63
Gold	40.23	. . .	. . .	40.99
Chlorine . .	29.07	. . .	. . .	29.50
Water . . .	2.32	2.37*	2.20*	1.87
	98.86			

	Found.		Calculated for $CsAuBr_4$.
Cæsium . . .	20.73	. . .	20.45
Gold . . .	30.32	30.26	30.34
Bromine . .	49.31	. . .	49.21
	100.36		

	Found.	Calculated for $RbAuCl_4$.
Rubidium . .	. . .	20.14
Gold	45.53	46.46
Chlorine . .	32.98	33.40

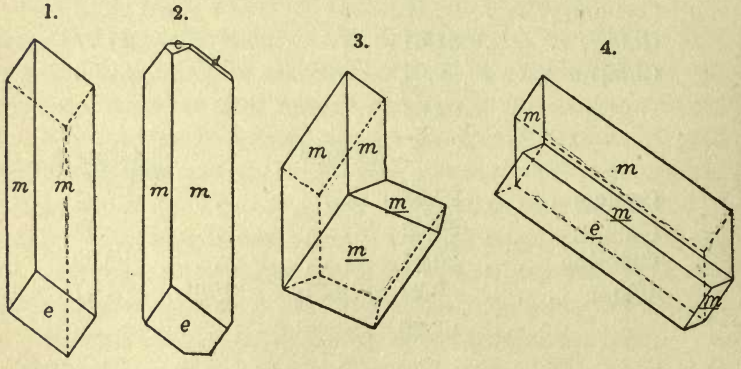
	Found.	Calculated for $RbAuBr_4$.
Rubidium . .	. . .	14.18
Gold	32.54	32.73
Bromine . .	. . .	53.08

* From a separate product.

Crystallography.

The crystallization of $CsAuCl_4$, $CsAuBr_4$, $RbAuCl_4$, and $RbAuBr_4$ is monoclinic. The four salts form an isomorphous group and are identical in crystalline habit. The forms which have been observed on them are:

c, 001, O	*d*, 021, 2-$\bar{\imath}$	*p*, $\bar{1}11$, I
m, 110, I	*e*, $\bar{2}01$, 2-$\bar{\imath}$	



The crystals are prismatic and are usually terminated by *e*, Fig. 1. When other faces are present, they are always small, as represented in Fig. 2. The pyramid *p*, which is not shown in the figure, frequently occurs as a small face, replacing the edge between *d* and *e*. Among the crystals of $CsAuBr_4$ several twins were observed, having *p*, $11\bar{1}$ as the twinning plane, Fig. 3, while Fig. 4 represents a crystal of $RbAuBr_4$ twinned about *e*, $20\bar{1}$. The letters belonging to the parts in twin position are underlined. Both kinds of twins are abnormally developed, as represented in the figures. In all four compounds the cleavage is perfect, parallel to the base.

The rubidium salts, being the most soluble, form readily in large crystals, several centimeters in length. The chloride, especially, yielded magnificent crystals, which frequently were only limited in length by the size of the vessel and volume of the solution containing them. The cæsium salts are less solu-

ble and were made in small prisms, seldom over 5 mm. in length. The crystals were frequently hollow or cavernous at the extremities; this was especially true of the two bromides. The faces, for the most part, gave excellent reflections of the signal on the goniometer.

The axial ratios are as follows:

$CsAuCl_4$
$\dot{a} : \bar{b} : c = 1.1255 : 1 : 0.7228$
$\beta = 71° 36'$

$CsAuBr_4$
$\dot{a} : \bar{b} : \dot{c} = 1.1359 : 1 : 0.7411$
$\beta = 70° 24\frac{1}{2}'$

$RbAuCl_4$
$\dot{a} : \bar{b} : \dot{c} = 1.1954 : 1 : 0.7385$
$\beta = 75° 32'$

$RbAuBr_4$
$\dot{a} : \bar{b} : \dot{c} : = 1.1951 : 1 : 0.7256$
$\beta = 76° 53\frac{1}{2}'$

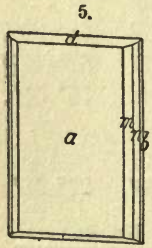
In the following tables the angles which were chosen as fundamental are marked by an asterisk:

	$CsAuCl_4$		$CsAuBr_4$	
	Measured.	Calculated.	Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$ =	*93° 46′	. . .	*93° 53′	. . .
$m \wedge c$, $110 \wedge 001$ =	77° 36′	77° 32′	*76° 46′	. . .
$m \wedge d$, $110 \wedge 021$ =	44° 6′	44° 7′	43° 23′	43° 20′
$d \wedge p$, $021 \wedge \bar{1}11$ =	. . .	. . .	32° 23′	32° 40½′
$d \wedge e$, $021 \wedge \bar{2}01$ =	*75° 17′	. . .	75° 31′	75° 59′
$m \wedge e$, $1\bar{1}0 \wedge \bar{2}01$ =	*60° 36′	. . .	*60° 41′	. . .
$c \wedge e$, $001 \wedge \bar{2}01$ =	64° 20′	64° 18′	. . .	. . .
$m \wedge m$, Re-entrant angle of twin,			27° 58′	27° 58′

	$BbAuCl_4$		$RbAuBr_4$	
	Measured.	Calculated.	Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$ =	*98° 21′	. . .	*98° 40′	. . .
$m \wedge c$, $110 \wedge 001$ =	*80° 36′	. . .	*81° 30′	. . .
$m \wedge d$, $110 \wedge 021$ =	. . .	. . .	44° 57′	45° 12½′
$d \wedge p$, $021 \wedge \bar{1}11$ =	. . .	. . .	31° 26′	31° 35½′
$d \wedge e$, $021 \wedge \bar{2}01$ =	. . .	. . .	72° 28′	72° 26′
$m \wedge e$, $1\bar{1}0 \wedge \bar{2}01$ =	*62° 12′	. . .	62° 9′	62° 21½′
$c \wedge e$, $001 \wedge \bar{2}01$ =	60° 4′	59° 59′	. . .	. . .
$d \wedge d$, $021 \wedge 0\bar{2}1$ =	110° 20′	110° 4½′	*109° 26′	. . .
$m \wedge m$, Re-entrant angle of twin,			55° 42′	55° 17′

In their axial ratios the two cæsium salts are very similar, as are also the two rubidium salts, while the rubidium com-

pounds differ considerably from those of cæsium, especially in the relation of $\dot{a}$ to the other axes and in the angles β. It is therefore evident that the replacement of one metal by another in these salts has a considerable influence upon their form, whereas, as we have shown, such a replacement in the cæsium and rubidium trihalides has little or no effect. There seems to be no regularity in the influence of the replacement of chlorine by bromine in these gold salts, for in the cæsium compounds the chloride has a slightly shorter axis $\dot{c}$ and a greater angle β than the bromide, while in the rubidium salts exactly the reverse is true in both cases. This unexpected relation between the chlorides and bromides has been confirmed by repeating the measurements, especially of the angle $m \wedge c$, using both crystal and cleavage faces. It is certain that this angle is about a degree greater with the chloride than with the bromide in the cæsium salts, while in the rubidium compounds it is about a degree less.



The crystallization of $2CsAuCl_4.H_2O$ is orthorhombic. This salt was repeatedly made, but only one crop of crystals was obtained which was suitable for measurement. These were thin plates, having the habit shown in Fig. 5. They were not over 5 mm. in length and were only a fraction of a millimeter thick. On removal from the mother-liquor or from a moist atmosphere, the transparent plates rapidly became opaque and the faces lost their lustre, so that only approximate measurements could be obtained.

The forms which were observed are:

a, 100, i-$\bar{i}$	*m*, 110, I	*d*, 101, 1-$\bar{i}$
b, 010, i-$\check{\imath}$	*n*, 120, i-$\breve{2}$	

The axial ratio is as follows:

$$\check{a} : \check{b} : \dot{c} = 0.625 : 1 : 0.24$$

The following measurements were made:

$a \wedge m$, $100 \wedge 110$ = about 32° $\quad a \wedge b$, $100 \wedge 010$ = about 90°
$a \wedge n$, $100 \wedge 120$ = about 51° $\quad d \wedge d$, $101 \wedge \bar{1}01$ = about 42°

Under the polarizing microscope the crystals show parallel extinction and, in convergent light, an acute bisectrix normal to a, 100. The plane of the optical axes is the base. The divergence of the axes is large, the hyperbolæ opening out beyond the field of the microscope. The axes of elasticity are:

$$\breve{a} = \mathfrak{c}, \qquad \bar{b} = \mathfrak{a}, \qquad \dot{c} = \mathfrak{b}.$$

The double refraction is therefore positive.

The change which the crystals undergo when exposed to dry air is a molecular rearrangement, accompanied by loss of water and probably a change to the anhydrous salt which was described above. This rearrangement is a beautiful sight when studied with the microscope in polarized light. The change commences a few minutes after the crystals are removed from the mother-liquor, and in less than ten minutes has usually advanced to such an extent that the crystals are no longer transparent. The crystals at first show a uniform action on polarized light; then from different parts of the surface the rearrangement, which is marked by aggregate polarization, commences. It advances, shooting out in various directions in a manner resembling the growth of ammonium chloride crystals under the microscope, until the whole field is covered and light is finally no longer transmitted.

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1892.

ON THE CÆSIUM-MERCURIC HALIDES.*

By H. L. WELLS.

It is to be expected that more complete series of double halides can be made with cæsium than with the other alkali metals, because it is the extreme member of the potassium group and the most electro-positive element known, and because cæsium double salts in general are less soluble than the corresponding compounds of the other alkali metals. A thorough study of these compounds seems desirable, since very little work has been done in this direction, and therefore the present investigation of the cæsium-mercuric chlorides, bromides, and iodides has been undertaken.

The following is a complete list of the previously described mercuric double halides containing the alkali metals and ammonium, as far as I have been able to find them:

Na_2HgCl_4	NH_4HgCl_3	$RbHg_2Cl_5$
Rb_2HgCl_4	$RbHgCl_3$	$KHg_2Cl_5.2H_2O$
Cs_2HgCl_4	$KHgBr_3$	. . . . .
$(NH_4)_2HgBr_4$	$NH_4HgCl_3.\frac{1}{2}H_2O$	. . . . .
K_2HgBr_4	$KHgCl_3.H_2O$	$(NH_4)_2Hg_3Cl_8.4H_2O$
Na_2HgI_4	$KHgBr_3.H_2O$	. . . . .
K_2HgI_4	$NaHgCl_3.1\frac{1}{2}H_2O$	. . . . .
$(NH_4)_2HgCl_4.H_2O$	$NH_4HgI_3.1\frac{1}{2}H_2O$	$(NH_4)_2Hg_9Cl_{20}$
$K_2HgCl_4.H_2O$	$KHgI_3.1\frac{1}{2}H_2O$	. . . . .
$Rb_2HgCl_4.2H_2O$	. . . . .	. . . . .
$(NH_4)_2HgI_4.3H_2O$	. . . . .	. . . . .

The greater number of these arrange themselves into two types with varying water of crystallization or with none. There are two compounds of a third type, while the two re-

* Amer. Jour. Sci., xliv, September, 1892.

maining, more complicated salts, stand alone. The last two were described by Holmes.*

An effort has been made to make the examination of the cæsium-mercuric salts very complete, but it is not safe to say that every possible compound has been prepared, for negative results are uncertain. It will not be necessary to describe the unsuccessful experiments where mixtures or uncertain products were obtained. It is sufficient to say that other double halides were repeatedly looked for in every direction, and every indication of a new salt was followed up until a homogeneous product was obtained and analyzed.

The following table gives a list of the salts that are to be described. One of them, Cs_2HgCl_4, has already been prepared by Godeffroy.†

I.	II.	III.
Cs_3HgCl_5	Cs_2HgCl_4	$CsHgCl_3$‡
Cs_3HgBr_5	Cs_2HgBr_4	$CsHgBr_3$‡
Cs_3HgI_5	Cs_2HgI_4	$CsHgI_3$
$Cs_3HgCl_3Br_2$	$Cs_2HgCl_2Br_2$	$CsHgClBr_2$‡
$Cs_3HgBr_3I_2$	$Cs_2HgBr_2I_2$‡	$CsHgBrI_2$
. . . . .	$Cs_2HgCl_2I_2$	. . . .
IV.	**V.**	**VI.**
. . . . .	$CsHg_2Cl_5$	$CsHg_5Cl_{11}$
. . . . .	$CsHg_2Br_5$	. . . .
$Cs_2Hg_3I_8$	$CsHg_2I_5$	. . . .
. . . . .	$CsHg_2ClBr_4$	$CsHg_5ClBr_{10}$

These salts confirm the composition of all the previously known alkaline-mercuric halides, as given in the preceding table, except the single compound $(NH_4)_2Hg_9Cl_{20}$. It is extremely probable, however, that the correct formula for this is $NH_4Hg_5Cl_{11}$, for Holmes obtained results slightly lower than his theory in his ammonium determinations, and it would be scarcely possible to distinguish between the two formulas by analysis, as will be seen from the following numbers:

* Chem. News, v, 351. † Berichte, viii, 9.

‡ These compounds are dimorphous.

	Calculated for $(NH_4)_2Hg_9Cl_{20}$.	Calculated for $NH_4Hg_5C_{11}$.	Differences.
Mercury	70.70	71.00	0.30
Ammonium	1.41	1.27	0.14

The differences between the amounts of mercury and cæsium for the corresponding formulas are 0.80 and 0.85, so that it is evident that the cæsium compound furnishes a far better means of determining the composition of the salts.

The first type, Cs_3HgHl_5, is a new one. These compounds are interesting as exceptions to Remsen's law concerning the composition of double halides.*

The salt $Cs_2Hg_3I_8$, although standing alone among the cæsium compounds, is a very well characterized body, and the compound $(NH_4)_2Hg_3Cl_8.4H_2O$, made by Holmes, belongs to the same type.

The results of the work on the cæsium-mercuric salts fulfil the expectations concerning the value of cæsium as a means of studying alkaline double halides, for all the previously discovered types have been made with this metal, and one besides that had never been discovered.

Preparation.

The compounds were made by dissolving mercuric halides in hot solutions of cæsium halides and cooling, or in some cases evaporating at ordinary temperatures, to crystallization. The relative amounts of the two halides and the dilution both have an important influence in determining the salt produced. In most cases dilution with water is equivalent to the addition of mercury, while concentration produces the same effect as the addition of a cæsium halide. It has been noticed, where more than one salt is deposited from a solution by cooling, that the salts with more mercuric halides are formed first. This shows that cooling a solution may be equivalent to the addition of cæsium.

There are only a few of the salts that can be recrystallized unchanged from water, most of them requiring the presence of

* Amer. Chem. Jour., xi, 296; xiv, 85.

an excess of cæsium halide, or in two or three cases mercuric halide, for their formation. Crystallization from water can therefore often be used for preparing one salt from another.

All the compounds were made with solutions of the normal salts without the use of acids. Some of them have been made with alcoholic solutions, but this solvent has not been found to possess any advantages except for preparing $CsHg_2I_5$.

Analytical Methods.

The salts were always carefully examined to be sure that they were not mixtures. Many mixed crops of crystals were obtained, but I am confident that the products analyzed were pure. The crystals for analysis were always quickly and thoroughly freed from the mother-liquor by pressing repeatedly between smooth filter-papers, and at the same time they were crushed to remove included liquid. During this drying process the substances were exposed to the air as little as possible to avoid any evaporation of the adhering liquid before its removal. After the products had been dried as thoroughly as possible in this way, they were usually exposed to the air for an hour or two to remove the last traces of moisture, but this was not done in a few cases where I wished to be certain that no easily lost water of crystallization was present.

Portions of about one gram of substance were usually taken for analysis. In no case was the analysis hampered from lack of material. The chlorides and bromides were readily dissolved in water, but it was necessary in analyzing the iodine compounds to dissolve them in water containing alcohol. Mercury was invariably determined as sulphide, the precipitate being collected, dried at 100°, and weighed on an asbestos filter in a Gooch crucible. Cæsium was usually determined in the filtrate from the mercuric sulphide and was always weighed as sulphate. In this operation the excess of sulphuric acid was removed by ignition in a current of air containing ammonia, as suggested by Krüss for potassium sulphate. In some cases where cæsium alone was to be determined, the substance was weighed out directly into a platinum crucible, sulphuric acid

was added, the excess of this and the mercury were removed by evaporation and heating, and normal cæsium sulphate was weighed. The halogens were invariably determined in separate portions and were weighed as silver salts. In the cases where two were present, they were determined by heating the mixed silver halides to constant weight in chlorine.

The Double Chlorides.

These are all white in color and are permanent when exposed to the air. On recrystallizing from water all of them finally yield $CsHgCl_3$.

Cs_3HgCl_5 is made by dissolving a comparatively small quantity of mercuric chloride in a nearly saturated cæsium chloride solution. It is deposited on cooling, but the best crystals are obtained by spontaneous evaporation. If too much of the mercuric compound is added or if too much water is present, other double salts or mixed products will be obtained. On the other hand, if too little mercuric chloride is present, cæsium chloride crystallizes out. The limits of the conditions under which it is formed are narrow, but by repeated trials, with slight variations suggested by previous results, a pure product is readily obtained. It forms slender, radiating prisms which are easily distinguished from the compounds with which it is liable to be mixed.

The following analysis was made of a sample which was rapidly dried on paper, but not air-dried. The small amount of water found was probably simply moisture. It was determined by direct weighing in a calcium-chloride tube.

	Found.	Calculated for Cs_3HgCl_5.
Cæsium . . .	51.15	51.38
Mercury . . .	24.84	25.76
Chlorine . . .	21.79	22.86
Water . . .	1.69	0.00
	99.47	100.00

Cs_2HgCl_4 is produced, by cooling a hot solution, when a little more mercuric chloride or water is used than in the case

of the last salt. The conditions for its formation are narrow. It forms large but usually very thin plates, which are readily distinguished from the other double chlorides. A sample was dried on paper for analysis.

	Found.	Calculated for Cs_2HgCl_4.
Cæsium . . .	44.06	43.75
Mercury . . .	. . .	32.90
Chlorine . . .	22.87	23.35
Water	0.52	0.00
		100.00

$CsHgCl_3$ is dimorphous, forming, according to circumstances, cubic or orthorhombic crystals. The cubic form is produced under widely varying conditions by cooling dilute aqueous solutions, when cæsium chloride is considerably in excess. The orthorhombic form is deposited when cæsium chloride is not in great excess, and by one or more recrystallizations from water of all the double chlorides. This form can be recrystallized from water indefinitely.

The compound is practically insoluble in absolute alcohol, but it dissolves in alcohol diluted with about one-third of its volume of water, and it is remarkable that the *cubic form* is deposited from such a solution on cooling.

The cubes often form peculiar aggregates, apparently of a pyramidal shape. The orthorhombic crystals are very brilliant and highly modified, usually forming groups of spear-shaped individuals joined end to end.

Three samples were analyzed: A, cubes simply dried on paper; B cubes from alcohol; C, orthorhombic crystals, air-dry.

	Found.			Calculated for $CsHgCl_3$.
	A.	B.	C.	
Cæsium . . .	30.29	30.26	29.92	30.26
Mercury . . .	44.80	. . .	45.63	45.51
Chlorine . . .	23.40	. . .	24.03	24.23
Water . . .	1.42	. . .	. . .	0.00
	99.91		99.58	100.00

Since the orthorhombic form of this compound is not decomposed by water, its solubility could be determined. This was done by analyzing the mother-liquor from a third recrystallization at about 17°. Of this solution, 100 parts contained 0.4255 parts of cæsium, corresponding to 1.406 parts of $CsHgCl_3$.

$CsHg_2Cl_5$ was made by dissolving 24 g. of $CsHgCl_3$ and 16 g. of $HgCl_2$ (a little more than one molecule of the latter) in about 150 c. c. of hot water and cooling. A large crop of needles was obtained which were undoubtedly homogeneous.

	Analysis gave	Calculated for $CsHg_2Cl_5$.
Cæsium . . .	18.13	18.72
Mercury . . .	56.32	56.30
Chlorine . . .	24.68	24.98
	99.13	100.00

The salt is not very readily decomposed by water, but by repeated recrystallization the orthorhombic form of $CsHgCl_3$ is obtained.

$CsHg_5Cl_{11}$ was prepared by making a nearly saturated solution of 12.5 g. of $HgCsCl_3$ and 38.5 g. of $HgCl_2$ (about one molecule of CsCl to six of $HgCl_2$) in boiling water and cooling. The compound was obtained in prisms, so well formed that there was no doubt about their homogeneity. Two crops were analyzed.

	Found.		Calculated for $CsHg_5Cl_{11}$.
Cæsium . .	8.68	8.51	8.73
Mercury . .	65.59	. . .	65.64
Chlorine . .	24.97	. . .	25.63
	99.24		100.00

A single recrystallization of this salt from water gave a mixed crop of crystals, and this, on repeating the operation, gave $CsHg_2Cl_5$, still containing a little of the original compound. This last crop was analyzed.

	Found.	Calculated for $CsHg_2Cl_5$.
Cæsium . . .	15.57	18.72

The Double Bromides.

All of these salts are white, or nearly so, except $CsHgBr_3$, which has a lemon-yellow color. This color is remarkable, since CsBr and $HgBr_2$ are both pure white.

All of the double bromides yield $CsHg_2Br_5$ on recrystallizing them one or more times from water. It is to be noticed that this salt belongs to a different type from the double chloride which is stable with water, but if alcohol is used for recrystallizing this bromide, the salt corresponding to the chloride just mentioned is deposited.

Cs_3HgBr_5.—The preparation of this salt is exactly analogous to that of the corresponding chloride, and it has the same appearance.

	Found.	Calculated for Cs_3HgBr_5.
Cæsium . . .	39.83	39.94
Mercury . . .	19.50	20.02
Bromine . . .	39.60	40.04
	98.93	100.00

Cs_2HgBr_4 is prepared similarly to the chloride, but the limits of the conditions under which it is formed are much wider. Like the chloride it usually forms very thin plates, but they can sometimes be produced of sufficient thickness for measurement. Three separate crops, made under considerably different conditions, were analyzed.

	Found.			Calculated for Cs_2HgBr_4.
Cæsium	33.84	34.43	33.69	33.84
Mercury	25.68	25.11	25.45	25.45
Bromine	40.48	40.40	40.52	40.71
	100.00	99.94	99.66	100.00

$CsHgBr_3$. — This compound is dimorphous, but while one form is cubic, like one of the chlorides, the other is monoclinic and has no apparent relation to the orthorhombic chloride. Just as in the case of the chlorides, the cubic form is produced when an excess of the cæsium halide is present, while the second form is deposited when this excess is not as

great. Unlike the corresponding chloride, the second form of the bromide is decomposed by recrystallization from water, the salt $CsHg_2Br_5$ being formed, but, as will be noticed beyond, the opposite transformation can be produced by recrystallizing the last-mentioned salt from alcohol. The limits of formation of the cubic salt are wide, but it is difficult to produce the other form in a pure state, and it is possible that the monoclinic crystals analyzed were mixed with a small quantity of the cubes.

	Found.		Calculated for $CsHgBr_3$.
	Cubic.	Monoclinic.	
Cæsium . . .	23.18	22.89	23.21
Mercury . . .	34.95	35.54	34.90
Bromine . . .	41.70	41.63	41.89
	99.83	100.06	100.00

$CsHg_2Br_5$. — The recrystallization of any of the other double bromides from water produces this salt, and it can be recrystallized indefinitely without decomposition. It forms very small, thin plates which have a very faint tinge of yellow. By spontaneous evaporation of a mother-liquor from a recrystallization of this salt somewhat larger crystals were formed. Three separate crops were analyzed.

	Found.			Calculated for $CsHg_2Br_5$.
Cæsium . . .	14.60	14.69	13.24	14.26
Mercury . . .	42.71	. . .	. . .	42.87
Bromine . . .	42.55	. . .	. . .	42.87
	99.86			100.00

The mother-liquor from a third recrystallization from water at about 16° was found to contain 0.1151 per cent of cæsium, corresponding to solubility of 0.807 parts of $CsHg_2Br_5$ in 100 parts of the solution. The salt dissolves rather sparingly in hot, strong alcohol and, on cooling this solution, the compound $CsHgBr_3$ separates out.

	Found.	Calculated for $CsHgBr_3$.
Cæsium . . .	22.68	23.21

The crystals thus obtained were not large enough to measure, but it was probable, from microscopic examination, that they were the monoclinic form of this compound. This is interesting from the fact that it is the cubic form of $CsHgCl_3$ which crystallizes from alcoholic solutions.

No satisfactory crops of crystals were obtained from solutions made with $CsHg_2Cl_5$ and $HgBr_2$, together.

The Double Iodides.

These salts are all yellow, $CsHg_2I_5$ and $Cs_2Hg_3I_8$ having a color nearly like that of normal potassium chromate, while the others become paler as the cæsium chloride increases. All of them are decomposed by water, forming compounds containing more mercuric iodide than the original salt, or, at last, mercuric iodide itself. It is therefore possible to take any one of these double salts, and, by recrystallizing from water and evaporating the resulting solutions, to prepare the complete series of five double iodides, as well as the component simple iodides, without the use of any new material. It is noticeable that the iodides differ from the chlorides and bromides in not including a salt that can be recrystallized continually from water. This peculiarity is doubtless due to the comparative insolubility of mercuric iodide. In most cases the analyses of the salts containing iodine show an excess of mercury and a deficiency of the halogen (or halogens). It is not known whether this was due to some impurity in the salts or to analytical errors. It is not considered probable that inaccuracies in the analyses could have caused so much variation from theory, for the methods used were the same as for the chlorides and bromides, except that alcohol was used as a solvent, and, while halogens and mercury were always determined in separate portions, the summations of the analyses were usually satisfactory.

Cs_3HgI_5. — This salt, like the corresponding chloride and bromide, requires for its preparation a very concentrated solution of the cæsium halide containing a relatively small amount of the mercuric compound. It crystallizes well and may be

obtained either by cooling or spontaneous evaporation. The crystals form peculiar, steep pyramids.

	Found.	Calculated for Cs_3HgI_5.
Cæsium . . .	33.02	32.33
Mercury . . .	16.33	16.21
Iodine	50.42	51.46
	99.77	100.00

Its specific gravity, taken in benzol, was found to be 4.605.

When this salt is dissolved in a small quantity of hot water, the compound Cs_2HgI_4 crystallizes out on cooling, but with a larger quantity of water everything remains in solution.

Cs_2HgI_4.— This salt is produced under wide limits of conditions by cooling solutions of the component salts when cæsium iodide is in excess. The monoclinic crystals vary in habit, forming long prisms, nearly square plates or intermediate forms. They are often obtained of very large size, sometimes extending completely across the bottom of the vessel containing the solution and turning upward at the ends besides.

	Found.		Calculated for Cs_2HgI_4.
Cæsium . . .	27.32	27.39	27.31
Mercury . . .	21.57	21.21	20.53
Iodine	51.41	51.49	52.16
	100.30	100.09	100.00

Two determinations of the specific gravity, taken in benzol, gave the numbers 4.799 and 4.812.

The salt is decomposed by water, giving, according to the quantity used, either one of the salts containing more mercuric iodide or mercuric iodide itself. It is not dissolved or decomposed by alcohol.

$CsHgI_3(.H_2O?)$.— This salt is formed only within very narrow limits from solutions containing a little more mercuric iodide or water than those from which the preceding salt is obtained. These conditions are perhaps most easily reached by dissolving the last salt in a small amount of hot water and cooling. It often happens that the three salts $Cs_2Hg_3I_8$,

$CsHgI_3$, and Cs_2HgI_4 are successively deposited as a solution cools, and it is consequently difficult to obtain the salt under consideration in a pure state, but this was accomplished after a great many trials with varying conditions. The compound forms very thin transparent plates which usually radiate from a point and are often of large size. By pressing on paper they rapidly become opaque. Whether this is caused by molecular rearrangement or loss of water of crystallization is not certain, for, on account of the extreme thinness of the crystals, it was impossible to decide whether a small amount of moisture or a molecule of very unstable water of crystallization was present. Two samples were analyzed. A was air-dried after pressing on paper; B was quickly dried on paper.

	Found. A.	Calculated for $CsHgI_3$.	Found. B.	Calculated for $CsHgI_3.H_2O$.
Cæsium . .	18.81	18.63	18.25	18.17
Mercury . .	29.29	28.01	28.74	27.33
Iodine . .	51.50	53.36	50.98	52.05
Water . . .	. . .	0.00	2.51*	2.45
	99.60	100.00	100.48	100.00

Like all the other iodides, this salt is decomposed by water.

$Cs_2Hg_3I_8$ is formed under widely different conditions. It is most convenient to prepare it by dissolving Cs_2HgI_4 in the proper amount of hot water and cooling. It is also formed, in a finely divided condition, by treating the same salt with not too much cold water. The crystals vary considerably in habit, but they can be readily distinguished from the other iodides. A characteristic form is a triangular plate, but plates of different shape and more or less elongated prisms often occur. The following analyses were made of separate crops. Sample C was made by treating Cs_2HgI_4 with cold water.

	Found. A.		B.	C.	Calculated for $Cs_2Hg_3I_8$
Cæsium . .	13.89	. . .	14.14	14.07	14.13
Mercury . .	33.76	. . .	. . .	33.83	31.88
Iodine . . .	52.07	52.10	52.63	52.96	53.99
	99.72			100.86	100.00

* By loss at 100°.

Specific gravity, taken in benzol, 5.14. The salt dissolves in alcohol. It is decomposed by water with the separation of a part of the mercuric iodide. From the solution thus obtained, the salts containing less mercuric iodide can be prepared by evaporation.

$CsHg_2I_5$. — When a hot aqueous solution of cæsium iodide is saturated with mercuric iodide, this compound is formed on cooling, but, under these conditions, the substance is usually mixed with HgI_2 and often with $Cs_2Hg_3I_8$. When weak alcohol is used as a solvent, however, a pure product is obtained without difficulty. It forms slender yellow prisms which become red on standing in an aqueous mother-liquor. They are more permanent in the solution when it is alcoholic, but, on drying them by pressing on paper, they quickly assume the red color of mercuric iodide without losing their form. It is probable that the spontaneous decomposition results in the formation of $Cs_3Hg_2I_8$ and HgI_2. It was necessary to analyze the material which had become red.

	Found.	Calculated for $CsHg_2I_5$.
Cæsium	11.47	11.39
Mercury	35.73	34.25
Iodine	52.93	54.36
	100.13	100.00

The Mixed Double Halides.

A great deal of labor has been devoted to a study of these compounds in order to find to what extent they could be prepared. The results show that cæsium chloride and mercuric bromide unite readily, although there is a tendency towards an exchange of halogens and the formation of unmixed salts. It is also noteworthy that, while there is a double chloride as well as a double bromide which is not decomposed by recrystallization from water, all the chloro-bromides finally yield mercuric bromide when so treated.

The number of bromo-iodides is less than that of the unmixed salts, for, when attempts are made to prepare com-

pounds containing the larger amounts of mercuric iodide, there is an exchange of halogens and almost pure double iodides are produced.

Only one compound of mercuric iodide with cæsium chloride could be prepared. This is $Cs_2HgCl_2I_2$, and the type to which it belongs may probably be considered, on this account, the most stable one of the cæsium-mercuric halides.

It is evident that the mixed salts are not as readily formed as the unmixed, and that the more dissimilar the two halogens are, the less tendency there is to form the mixed compounds.*

In preparing these salts, containing two different halogens, the halogen of higher atomic weight was always added in combination with the mercury. The methods of preparation are exactly analogous to those by which the unmixed salts are made, so that most of these details will be omitted in describing them.

The Chloro-bromides.

In form these all resemble the unmixed salts between which they are intermediate, and all of them are colorless except $CsHgClBr_2$, which is pale yellow.

$Cs_3HgCl_3Br_2$. —

	Found.	Calculated for $Cs_3HgCl_3Br_2$.
Cæsium	48.12	46.10
Mercury	23.80	23.11
Chlorine	16.24	12.30
Bromine	11.82	18.49
	99.98	100.00

The product was made with a very large excess of cæsium chloride, and it contained a considerable amount of the double chloride. The analysis corresponds nearly to the formula $2Cs_3HgCl_3Br_2 + Cs_3HgCl_5$.

$Cs_2HgCl_2Br_2$. — Two products, which were made under different conditions, were analyzed.

* This point is discussed in connection with the cæsium trihalides. (Wells and Penfield, Amer. Jour. Sci., III, xliii, 31 and 32.)

	Found.		Calculated for $Cs_2HgCl_2Br_2$.
Cæsium . . .	40.34	38.86	38.16
Mercury	28.79	28.58	28.69
Chlorine	12.94	10.48	10.19
Bromine	17.43	22.07	22.96
	99.50	99.99	100.00

One of these crops corresponds very closely to the formula, while the other, made in the presence of a greater excess of cæsium chloride, contains a little Cs_2HgCl_4.

$CsHgClBr_2$. — This has been obtained, like the chloride and bromide, in dimorphous forms. One of these is cubic like the other salts, while the second form crystallizes like the chloride and not like the bromide. The color of both varieties is pale yellow.

	Found.				Calculated for $CsHgClBr_2$.
	Cubic Form.	Orthorhombic Form. Separate Products.			
Cæsium . .	26.50	26.97	26.74	26.01	25.17
Mercury . .	38.75	40.21	40.05	38.91	37.84
Chlorine . .	9.23	11.32	11.42	8.53	6.72
Bromine . .	25.21	21.63	21.94	26.65	30.27
	99.69	100.13	100.15	100.10	100.00

These products evidently contain some of the chloride. The analyses of the first two samples of the orthorhombic salt correspond closely to the formula, $2CsHgClBr_2 + CsHgCl_3$.

$CsHg_2ClBr_4$. — Two separate products, made under different conditions, were analyzed.

	Found.		Calculated for $CsHg_2ClBr_4$.
Cæsium . . .	15.48	15.23	14.97
Mercury . . .	45.72	45.06	45.02
Chlorine . . .	5.75	3.71	3.99
Bromine . . .	32.30	36.06	36.02
	99.25	100.06	100.00

$CsHg_5ClBr_{10}$. — This compound was prepared by recrystallizing the preceding salt from water.

	Found.	Calculated for $CsHg_2ClBr_{10}$.
Cæsium . . .	6.23	6.76
Mercury . . .	52.77	50.80
Chlorine . . .	2.85	1.80
Bromine . . .	38.19	40.64
	100.04	100.00

There is a chloride corresponding to this compound, but no bromide was obtained of this type. It forms elongated crystals, much smaller than the chloride. The final product, when this salt is recrystallized from water, is mercuric bromide.

The Bromo-iodides.

Only three of these compounds have been prepared. When attempts were made to obtain compounds containing larger amounts of mecuric iodide, there was an interchange of halogens and nearly pure double iodides were formed. Two such products were analyzed.

	Found.	Calculated for $Cs_2Hg_3I_8$.	Found.	Calculated for $CsHg_2I_5$.
Cæsium . . .	14.69	14.13	11.62	11.39
Mercury . . .	33.72	31.88	36.09	34.25
Bromine . . .	2.19	0.00	2.43	0.00
Iodine	49.58	53.99	49.45	54.36
	100.18	100.00	99.59	100.00

$Cs_3HgBr_3I_2$. — This salt resembles the iodide, not the bromide, in form. Its color is a pale yellow, intermediate between the brighter iodide and the colorless bromide.

	Found.	Calculated for $Cs_3HgBr_3I_2$.
Cæsium . . .	37.21	36.50
Mercury . . .	19.39	18.30
Bromine . . .	25.18	21.96
Iodine	18.24	23.24
	100.02	100.00

$Cs_2HgBr_2I_2$. — This compound has a very faint tinge of yellow. It is apparently dimorphous, although no other salt

of this type has been made in more than one form. It occurs in very thin plates, like the chloride, bromide, and chlorobromide, and in stout monoclinic crystals like the iodide. The limits of the conditions under which the plates are made are very narrow, and it is difficult to obtain them free from the dimorphous crystals. As the solution cools, however, the plates are deposited first, and, with the proper dilution, it is possible to remove them and get the mother-liquor pressed out with paper before the other crystals begin to form. There is no difficulty in preparing the other modification of the compound.

	Found.		
	Thin Plates.	Orthorhombic Crystals.	Calculated for $Cs_2HgBr_2I_2$.
Cæsium . . .	30.71	30.20	30.23
Mercury . . .	24.14	23.86	22.73
Bromine . . .	21.05	17.91	18.18
Iodine	24.23	28.50	28.86
	100.13	100.47	100.00

It is noticable that the plates, which resemble the bromide in form, contain a small excess of bromine and a corresponding deficiency of iodine.

$CsHgBrI_2$. — Only one form of this compound has been prepared, although three other salts of this type are dimorphous. Its form is monoclinic, like one modification of the bromide, and it is pale yellow in color.

	Found.	Calculated for $CsHgBrI_2$.
Cæsium . . .	20.26	19.94
Mercury . . .	31.44	29.99
Bromine . . .	13.35	11.99
Iodine	34.39	38.08
	99.44	100.00

The Chloro-iodide, $Cs_2HgCl_2I_2$.

This is the only combination of cæsium chloride and mercuric iodide that could be produced. It is formed only in very concentrated solutions containing a great excess of

cæsium chloride. Its form is different from any other salt of the type, for it occurs in slender, radiating needles. It is snow-white in color, and when it is brought in contact with water it instantly becomes bright red from the formation of mercuric iodide. Two entirely separate crops were analyzed.

	Found.		Calculated for $CsHgCl_2I_2$.
Cæsium . . .	33.38	33.14	33.63
Mercury . . .	26.71	. . .	25.28
Chlorine . . .	8.87	9.01	8.98
Iodine	30.85	30.17	32.11
	99.81		100.00

When it was attempted to make a chloro-iodide containing more mercuric iodide than this, a nearly pure double-iodide was formed by exchange of halogens.

	Found.	Calculated for $Cs_2Hg_3I_8$.
Cæsium . . .	13.76	14.13
Mercury . . .	33.49	31.88
Chlorine . . .	0.16	0.00
Iodine	50.74	53.99
	98.15	100.00

The investigation of double halides will be continued in this laboratory, and it is hoped that a further study of the cæsium salts will lead to a better knowledge of this class of compounds in general than we now possess.

In conclusion, it gives me pleasure to express my gratitude to my colleague, Professor Penfield, for his hearty co-operation in undertaking the crystallographic examination of the compounds which have been described. His results have been freely used in the foregoing descriptions, and they will be given in detail in a future article.

SHEFFIELD SCIENTIFIC SCHOOL,
May, 1892.

ON THE CRYSTALLOGRAPHY OF THE CÆSIUM-MERCURIC HALIDES.*

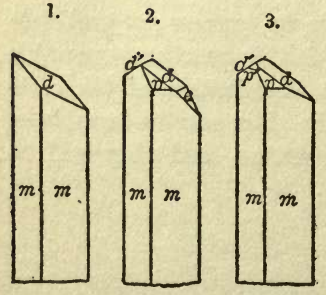
By S. L. PENFIELD.

THE salts to be described in this paper were prepared by Prof. H. L. Wells, and their chemical description has been given by him in the preceding paper.

The crystals were all measured on a Fuess reflecting goniometer, model II, and great pains were taken to select the best measurements as fundamental. In a few cases, where the crystals were very small and the reflections of the signal, therefore, rather broad, the mean of a series of measurements was used. The axial ratios are given in tabular form at the beginning of each separate chemical type, and the fundamental angles, from which these are derived, are marked by an asterisk in the table of angles accompanying each salt.

Type 3 : 1.

		$\breve{a} : \bar{b} : \dot{c}$
Cs_3HgCl_5	Orthorhombic, monoclinic hemihedrism	0.7976 : 1 : 0.6605
$Cs_3HgCl_3Br_2$	Orthorhombic, monoclinic hemihedrism	0.7882 : 1 : 0.6527
Cs_3HgBr_5	Orthorhombic, monoclinic hemihedrism	0.7966 : 1 : 0.6656
Cs_3HgI_5	Orthorhombic, sphenoidal hemihedrism	0.5362 : 1 : 0.97975
	or $\frac{2}{3}\breve{a} : \bar{b} : \frac{2}{3}\dot{c} =$	0.8043 : 1 : 0.6532
$Cs_3HgBr_3I_2$	Orthorhombic, sphenoidal hemihedrism	Approx. like Cs_3HgI_5



The first three salts have exactly the same habit and crystallize in slender prisms, attached at one end and terminated at the other by faces which are arranged with monoclinic symmetry, Figs. 1, 2, and 3. The crystals were seldom over 1 mm. in diameter, but the faces were perfect and admitted of accurate measurement. The forms and angles are:

* Amer. Jour. Sci., xliv, October, 1892.

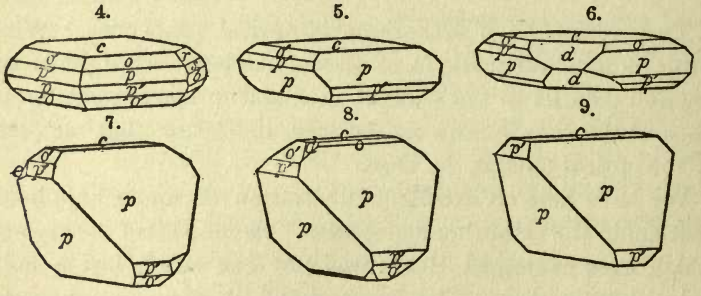
m, 110, *I* *d'*, 0$\bar{1}$1, '1-$\breve{\imath}$ *p*, 111, 1
d, 011, 1-$\breve{\imath}$ *e*, 021, 2-$\breve{\imath}$ *p'*, 1$\bar{1}$1, '1

	Cs_2HgCl_2. Measured.	Calculated.	$Cs_2HgCl_2Br_2$. Measured.	Calculated.	Cs_2HgBr_2. Measured.	Calculated.
$m \wedge m$, 110 $\wedge$ 1$\bar{1}$0 =	*77° 9′	. . .	76° 33′	76° 30′	*77° 5′	. . .
$m \wedge p$, 110 $\wedge$ 111 =	*43° 21′	. . .	*43° 29′	. . .	*43° 6½′	. . .
$m \wedge p$, 1$\bar{1}$0 $\wedge$ 111 =	80° 41′	80° 41½′	. . .	. . .	80° 37′	80° 36½′
$m \wedge d$, 110 $\wedge$ 011 =	69° 55′	69° 54′	70° 14′	70° 13′	69° 49′	69° 48′
$m \wedge e$, 110 $\wedge$ 021 =	60° 8′	60° 11′	. . .	. . .	60° 10′	60° 7′
$d \wedge e$, 011 $\wedge$ 021 =	19° 29′	19° 26′	19° 28′	19° 25′	. . .	. . .
$d \wedge d'$, 011 $\wedge$ 0$\bar{1}$1 =	66° 53′	66° 53½′	*66° 16′	. . .	67° 16′	67° 18′
$d \wedge p$, 011 $\wedge$ 111 =	34° 39′	34° 39′	34° 37′	34° 44′	34° 47′	34° 49′

The crystals have orthorhombic optical properties. When lying on their prismatic faces all show in polarized light an extinction parallel to the vertical axis, and in convergent light a trace of the ring system can be seen, indicating that the plane of the optical axes is the base.

We have here an excellent illustration of monoclinic hemihedrism in the orthorhombic system. Among all of the crystals which were examined, there was not one which had a holohedral termination. The forms *d'* and *p'*, when present, were always smaller than the corresponding forms *d* and *p*, while *e* was only observed to the right above. Also the right-handed vertical edge of the prism showed a tendency toward a skeleton-like growth, which was not observed to the left. In measuring the crystals great pains were taken to detect a monoclinic character by the angles, but none could be found. Of course the three salts may be regarded as monoclinic, with an angle β, differing so little from 90° that it cannot be detected by the goniometer; but against such a supposition are the arguments that the crystals have orthorhombic optical properties, and while there is a variation in the axial ratios of the series as bromine is substituted for chlorine, there is no change in the angle β, as would be expected if the salts were monoclinic. In this connection it is interesting to note that while the chloride and bromide are very similar in their axial ratios, the chemically intermediate chloro-bromide is not crystallographically intermediate.

At the present time there seems to be no other known compound which illustrates this hemihedrism. Different substances, which have been referred to this class, as datolite or wolframite, for example, have been shown by accurate measurement, or a study of their optical properties, to be truly monoclinic. Prof. P. Groth, in the last edition of his "Physikalische Krystallographie," has not mentioned this hemihedrism as a possibility in the orthorhombic system, although in the former edition of his work and in most treatises on crystallography it is recognized.



The different crops of Cs_3HgI_5 which were examined showed a great variety in habit, represented by Figs. 4–8. The hemihedral development is not always strongly marked, and forms like Figs. 5 and 6 are the commonest. The crystals sometimes measured over 5 mm. in diameter and gave excellent reflections.

Only one crop of $Cs_3HgBr_3I_2$ was examined. The crystals were in the form of sphenoids, Fig. 9, some of them over 10 mm. in diameter, but the faces were curved and striated and only approximate measurements could be made.

The forms which were observed are:

b, 010, i-$\breve{\imath}$	*d*, 102, $\frac{1}{2}$-$\bar{\imath}$	*s*, 021, 2-$\breve{\imath}$	*p*′ 1$\bar{1}$1,-1	*o*′, 1$\bar{1}$2,-$\frac{1}{2}$
c, 001, 0	*r*, 011, 1-$\breve{\imath}$	*p*, 111, 1	*o*, 112, $\frac{1}{2}$	*e*, 121,-2-$\breve{2}$

The angles of Cs_3HgI_5 are:

	Measured.	Calculated.
$c \wedge p$, $001 \wedge 111$ =	*64° 15′	. . .
$p \wedge p'$, $111 \wedge 1\bar{1}1$ =	*50° 23′	. . .
$c \wedge r$, $001 \wedge 011$ =	44° 23′	44° 25′
$c \wedge s$, $001 \wedge 021$ =	62° 58′	62° 58′

	Measured.	Calculated.
$c \wedge o$, $001 \wedge 112$ =	46° 1′	46° 2′
$o \wedge o'$, $112 \wedge 1\bar{1}2$ =	39° 55′	39° 46′
$o \wedge o'$, $112 \wedge 11\bar{2}$ =	87° 57′	87° 56′
$o \wedge d$, $112 \wedge 102$ =	19° 50′	19° 53′
$p \wedge e$, $1\bar{1}1 \wedge 121$ =	17° 48′	18° 4′

Both Cs_3HgI_5 and $Cs_3HgBr_3I_2$ cleave distinctly, parallel to the base, but the crystals are very brittle and usually break with a conchoidal fracture. Crystals of the former, which are tabular parallel to the base, show in convergent polarized light a bisectrix normal to *c*, 001; the plane of the optical axes is the macropinacoid, and their divergence is large.

Type 2 : 1.

		a : *b* : *c*	
Cs_2HgCl_4	Not measured.		
Cs_2HgBr_4	Orthorhombic	0.5706 : 1 : 1.4715	
$Cs_2HgCl_2Br_2$	Orthorhombic	0.567 : 1 : . . .	
$Cs_2HgCl_2I_2$	Orthorhombic	Not measured.	
Cs_2HgI_4	Monoclinic	1.3155 : 1 : 0.9260	$\beta = 69° 56'$
$Cs_2HgBr_2I_2$	Monoclinic	Approximately like Cs_2HgI_4.	

The crystals of Cs_2HgCl_4 were too thin to measure.

Both Cs_2HgBr_4 and $Cs_2HgCl_2Br_2$ crystallize in thin rectangular plates; those of the former were sometimes several centimeters long, but seldom over $\frac{1}{2}$ mm. thick, and had the habit shown in Fig. 10. The crystals of the latter salt were very much thinner. The plates were often grouped, with the large pinacoid faces slightly divergent, and isolated crystals, suitable for exact measurement, were only occasionally found.

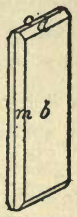


Fig. 10.

The forms which were observed on Cs_2HgBr_4 are:

b, 010, *i*-$\breve{\imath}$ *c*, 001, *O* *m*, 110, *I* *d*, 011, 1-$\breve{\imath}$ *p*, 221, 2

and on $Cs_2HgCl_2Br_2$, *b*, *m* and a second prism 130, *i*-$\breve{3}$. The end faces could not be made out.

The angles of Cs_2HgBr_4 are:

	Measured.		Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$	$= *59° 25'$	$m \wedge p$, $110 \wedge 221$	$= 33° 58\frac{1}{2}'$	$33° 58'$
$b \wedge d$, $010 \wedge 011$	$= *34° 12'$			

On this salt the dome *d* is always small and frequently wanting. The pyramid *p* was only observed on a few crystals. In convergent polarized light a bisectrix may be seen normal

to b, 010. The plane of the optical axes is the macropinacoid, and their divergence is so large that they cannot be measured in air, but in a-monobromnaphtaline the following values were obtained:

$2H = 80° 12'$ for yellow, Na flame.
$2H = 85° 23'$ for red, Li flame.

The dispersion is strong $\rho > v$. The acute bisectrix is axis of least elasticity, the double refraction is therefore positive.

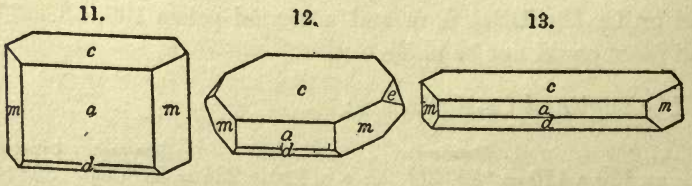
The only angles on $Cs_2HgCl_2Br_2$ which were measured are:

$m \wedge m$, $110 \wedge 1\bar{1}0 = *59° 6'$ and $110 \wedge 130 =$ approx. $30° 53'$, calculated $30° 59'$

In convergent polarized light a bisectrix may be seen normal to b, 010. The plane of the optical axes is the macropinacoid, and their divergence is large. The axis of greatest elasticity is normal to b.

Only very fine needles of $Cs_2HgCl_2I_2$ were obtained, which were too small for measurement. These appeared under the microscope as striated prisms, with their obtuse edges rounded by oscillatory combinations. In polarized light they show a parallel extinction, and in convergent light a biaxial interference figure, the plane of the optical axes being the vertical pinacoid. The acute bisectrix is axis of least elasticity.

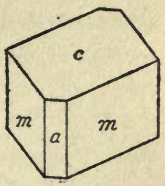
The crystals of Cs_2HgI_4, which were frequently several centimeters in diameter, showed a variety of habits represented



in Figs. 11, 12 and 13. The crystals of the latter habit are usually attached at one end and taper toward the free extremity, owing to a tendency to develop vicinal pyramids in the zone d–b.

The crystals of $Cs_2HgBr_2I_2$, which were examined, were about 2 mm. in diameter and had the simple habit shown in Fig. 14. The faces were rounded and uneven, so that only approximate measurements could be made.

14.



The forms and angles are:

a, 100, *i*-$\bar{i}$	*c*, 001, *O*	*d*, $\bar{2}01$, 2-$\bar{i}$
b, 010, *i*-$\bar{i}$	*m*, 110, *I*	*e*, 011, 1-$\bar{i}$

	Cs_2HgI_4. Measured.	Calculated.	$Cs_2HgBr_2I_2$. Measured approximately.
$c \wedge a$, 001, $100 =$	*69° 56′	. . .	66° 41′ to 66° 47′
$m \wedge m$, 110 $\wedge$ $\bar{1}10 =$	*77° 58′	. . .	77° 16′ to 77° 57′
$a \wedge d$, $\bar{1}00 \wedge \bar{2}01 =$	*41° 25′	. . .	. . . . .
$c \wedge e$, 001 $\wedge$ 011 =	40° 55′	41° 1′	. . . . .

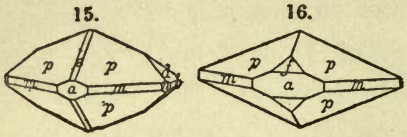
The cleavage of both salts is perfect parallel to the base, less so parallel to the clinopinacoid. With Cs_2HgI_4 the plane of the optical axes is at right angles to the symmetry plane, and clinopinacoid cleavage sections show in convergent polarized light an obtuse bisectrix, which is axis of least elasticity. The axis of greatest elasticity makes an angle of about 50° with the vertical axis in the acute angle β.

Type 1 : 1.

		a : *b* : *c*	
$CsHgCl_3$	Isometric and Orthorhombic	0.57735 : 1 : 0.40884	
$CsHgClBr_2$	Isometric and Orthorhombic	Approximately like the above.	
$CsHgBr_3$	Isometric and Monoclinic	1.0124 : 1 : 0.70715	$\beta = 87° 7′$
$CsHgBrI_2$	Monoclinic	0.978 : 1 : 0.743	$\beta = 87° 3\frac{1}{2}′$
$CsHgI_3$	Not measured.		

The first three compounds are dimorphous, and, from solutions containing an excess of alkali halide, they all crystallize in cubes. These sometimes have their edges truncated by small dodecahedron faces, less often bevelled by 210, *i*-2. The crystals show a slight action on polarized light and give an extinction parallel to the diagonals of the cube, but this anomaly is probably due to some internal tension, for when crushed the fragments are isotropic. No cleavage could be detected.

$CsHgCl_3$ was repeatedly recrystallized from water and always two types were observed. One of these was confined to those crystals which were attached to the sides of the beaker, while those which grew more in the interior had an entirely different habit. The crystals of the first type averaged about 2 mm. in greatest diameter and had the habit shown in Figs. 15 and 16. The forms and angles are as follows:



a, 100, i-$\bar{i}$	*m*, 110, *I*	*e*, 101, 1-$\bar{i}$	*d*, 021, 2-$\breve{i}$
b, 010, i-$\breve{i}$	*n*, 130, i-$\breve{3}$	*f*, 201, 2-$\bar{i}$	*p*, 111, 1

	Measured.	Calculated.		Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0 =$	*60° 0′	. . .	$a \wedge p$, $100 \wedge 111 = $	56° 45′	56° 45½′
$d \wedge d$, $021 \wedge 02\bar{1} =$	*101° 27½′	. . .	$m \wedge p$, $110 \wedge 111 = $	71° 33½′	71° 33′
$p \wedge p$, $111 \wedge \bar{1}11 =$	66° 28½′	66° 29′	$p \wedge d$, $111 \wedge 021 = $	36° 54′	36° 54′
$p \wedge p$, $111 \wedge 1\bar{1}1 =$	36° 54′	36° 54′	$a \wedge e$, $100 \wedge 101 = $	54° 42½′	54° 42′
$m \wedge p$, $110 \wedge 111 =$	50° 43½′	50° 43⅔′	$a \wedge f$, $100 \wedge 201 = $	35° 13′	35° 13½′

The crystals were brilliant and gave wonderful reflections. The prismatic angle was measured repeatedly and found to be 60°, and the forms *could* be referred to the hexagonal system, making the *m* and *b* faces a prism of the first order, *a* and *n* a prism of the second order, and *p* and *d* the unit pyramid. There was nothing, however, in the development of the faces to suggest hexagonal symmetry. Thin sections were prepared, hoping that the optical properties would throw some light upon the form, but they showed only a very weak double refraction, in fact they appeared almost like isotropic sections, so that no satisfactory conclusions could be drawn.

The crystals of the second type were spearhead-shaped, Fig. 17, and grew out into the centre of the solution, either attached to one another by the acute solid angles, or to a slender, parallel growth of crystals, which served as a sort of stem. The crystals which are about 5 mm. in length are complicated and perplexing, and the faces are developed with tri-

clinic symmetry, although they can be referred to the axes of the first type. The most prominent faces are shown in the figure, while the distribution of all those which gave distinct reflections are given in the spherical projection, Fig. 18. The forms which were observed are given as if they belonged to a triclinic crystal and are:

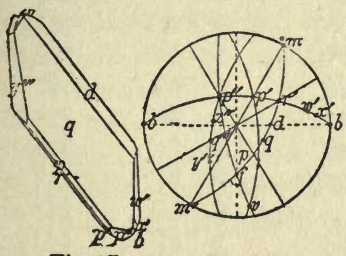


Fig. 17.

Fig. 18.

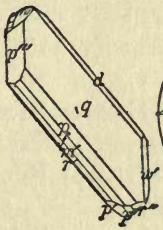


Fig. 19.

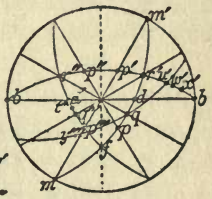


Fig. 20.

b, 010, *i*-$\check{\imath}$ *p*, 111, 1′ *q*‴, 1$\bar{3}$2, $'\frac{3}{2}$-$\check{3}$ *y*‴, 7$\bar{9}$5, $'\frac{9}{5}$-$\frac{\check{9}}{7}$
m′, 1$\bar{1}$0, ′*I* *p*′, $\bar{1}$11, ,1 *r*′, $\bar{1}$31, ,3-$\check{3}$ *z*″, $\bar{1}$97, $\frac{9}{7}$-$\check{9}'$
f, 201, ′2-$\check{\imath}$′ *p*″, $\bar{1}\bar{1}$1, 1, *q*, 132, $\frac{3}{2}$-$\check{3}'$ *w*, $\bar{1}$91, ,9-$\check{9}$ *x*′, $\bar{1}$151, ,15-$\check{1}5$ *v*, 1131, $11\frac{1}{3}'$
d, 021, 2-$\check{\imath}$″

The crystals gave excellent reflections, and only occasionally a slight striation interfered with making accurate measurements. All of the forms were observed on two crystals, and probably others could have been found by measuring a larger number.

The crystals of $CsHgClBr_2$ have a similar habit, Fig. 19, and the distribution of all of the faces which gave distinct reflections is given in the spherical projection, Fig. 20. This salt is more insoluble than the chloride, and the crystals are consequently much smaller, not over $1\frac{1}{2}$ mm. in greatest diameter. All of the forms given above for the chloride were observed except *z* and *v*, and in addition:

d′, 0$\bar{2}$1, ′2-$\check{\imath}$ *p*‴, 1$\bar{1}$1, ′1 *r*″, $\bar{1}$31, 3-$\check{3}$, *u*′, I71, 7-$\check{7}$ *t*, 2$\bar{1}$27, $'\frac{2}{7}$-$\check{6}$

The crystals gave very good reflections, considering their size, and the best measurements agreed so well with those of

the chloride that no attempt was made to calculate a new axial ratio. The most marked difference in the two salts is the development of the zone p'' z'' q''' y''' in the chloride and r'' d' t''' q''' p''' f in the chlorobromide.

The measured and calculated angles are as follows:

		$CsHgCl_3$.	$CsHgClBr_2$.	Calculated.
m' ∧ f,	$1\bar{1}0$ ∧ 201	44° 45′	45° 6′	44° 58⅓′
f ∧ p,	201 ∧ 111	26° 35′	26° 27′	26° 34⅓′
p ∧ q,	111 ∧ 132	18° 27′	18° 34′	18° 27′
q ∧ d,	132 ∧ 021	18° 26′	18° 23′	18° 27′
d ∧ r,	021 ∧ $\bar{1}31$	26° 44′	26° 26′	26° 34½′
x ∧ r,	$\bar{1}151$ ∧ $\bar{1}31$	33° 40′	33° 20′	33° 40½′
w ∧ r,	$\bar{1}91$ ∧ $\bar{1}31$	26° 36½′	26° 27′	26° 33′
u ∧ r,	$\bar{1}71$ ∧ $\bar{1}31$	. . .	21° 35′	21° 47½′
r ∧ p',	$\bar{1}31$ ∧ $\bar{1}11$	26° 33′	26° 37′	26° 34½′
p' ∧ p'',	$\bar{1}11$ ∧ $\bar{1}\bar{1}1$	36° 52½′	36° 37′	36° 54′
b ∧ r'',	$0\bar{1}0$ ∧ $\bar{1}31$	44° 44′	. . .	44° 58′
y''' ∧ q''',	$7\bar{9}5$ ∧ $1\bar{3}2$	22° 13′	. . .	22° 13′
z'' ∧ p'',	$\bar{1}97$ ∧ $\bar{1}\bar{1}1$	28° 38′	. . .	28° 35′
q''' ∧ p'',	$1\bar{3}2$ ∧ $\bar{1}\bar{1}1$	50° 54′	. . .	50° 49′
y''' ∧ q,	$7\bar{9}5$ ∧ 132	62° 29½′	62° 22′	62° 28½′
p'' ∧ v,	$\bar{1}\bar{1}1$ ∧ $\bar{1}\bar{1}3\bar{1}$	60° 46′	. . .	60° 45′
p' ∧ v,	$\bar{1}11$ ∧ $\bar{1}\bar{1}3\bar{1}$	66° 53′	. . .	66° 59′
f ∧ p''',	201 ∧ $1\bar{1}1$	. . .	26° 38′	26° 34½′
p''' ∧ q''',	$1\bar{1}1$ ∧ $1\bar{3}2$	. . .	18° 23′	18° 27′
q''' ∧ d',	$1\bar{3}2$ ∧ $0\bar{2}1$	. . .	18° 34′	18° 27′
t''' ∧ d',	$2\bar{1}\bar{2}7$ ∧ $0\bar{2}1$	. . .	10° 13′	10° 19′
q ∧ w,	132 ∧ $\bar{1}91$	50° 59′	51° 4′	50° 46′
q ∧ p''',	132 ∧ $1\bar{1}1$	. . .	50° 50′	50° 49′
q ∧ q''',	132 ∧ $1\bar{3}2$	60° 3′	. . .	60° 4′

It will be seen from the spherical projection that the forms of $CsHgClBr_2$ lie mostly in three zones, suggestive of hexagonal rhombohedral symmetry, although there is nothing in the arrangement of the faces, and still less with $CsHgCl_3$, to indicate that this is correct. The crystals of $CsHgClBr_2$ have a slightly stronger action on polarized light than those of $CsHgCl_3$. When lying on the large q faces, both show an extinction parallel to the edges between p, q and d.

On a crystal of $CsHgCl_3$ the faces in the zone *p*, *q*, *d*, *r* made prisms, which served for the determination of the following indices of refraction:

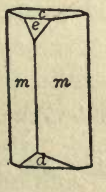
Prism of 36° 54′, 021 ∧ $\bar{1}\bar{1}\bar{1}$, *n*, *y*, Na flame = 1.791 *n*, *r*, Li flame = 1.779
Prism of 63° 28½′, $\bar{1}31 \wedge \bar{1}1\bar{1}$, *n*, *y*, " " = 1.792 *n*, *r*, " " = 1.779

The crystal was of course very small and the refracted rays were not very bright, but the latter were well defined and the double refraction was not strong enough to separate them into two distinct rays.

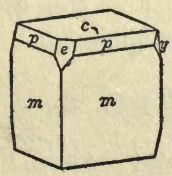
The author cannot give any satisfactory explanation of these curious forms. They seem to illustrate a tetartohedral development of the faces of an orthorhombic crystal, resulting in a figure with triclinic symmetry. The mathematical relations have been very carefully determined and the facts given. It is hoped that a further study will throw some light on the subject.

The different crops of $CsHgBr_3$ which were examined showed a variety of habits, represented by Figs. 21, 22, and 23.

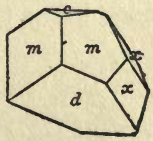
21.



22.



23.



The forms and angles are as follows:

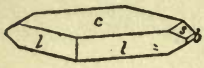
c, 001, 0	*e*, 201, —2-$\bar{1}$	*o*, $\bar{1}11$, 1	*y*, 261, —6-$\dot{3}$
m, 110, *I*	*d*, $\bar{1}01$, 1-$\bar{1}$	*p*, 221, —2	*x*, $\bar{1}31$, 3-$\dot{3}$

	Measured.	Calculated.		Measured.	Calculated.
$c \wedge m$, $001 \wedge 110$ =	*87° 58½′	. . .	$m \wedge m$, $110 \wedge \bar{1}10$ =	*90° 38′	. . .
$c \wedge d$, $001 \wedge \bar{1}01$ =	*35° 52′	. . .	$d \wedge x$, $\bar{1}01 \wedge \bar{1}31$ =	60° 41′	60° 40′
$c \wedge e$, $001 \wedge 201$ =	52° 28½′	52° 30½′	$e \wedge p$, $201 \wedge 221$ =	38° 46′	38° 46½′
$c \wedge o$, $001 \wedge \bar{1}11$ =	45° 40′	45° 49′	$e \wedge y$, $201 \wedge 261$ =	67° 21′	67° 28′

The crystals are seldom over 5 mm. in diameter and sometimes have a hemimorphic development, although this is not

always apparent. In the prevailing type, Fig. 22, there is perhaps a tendency for 221 to predominate over $2\bar{2}1$, but this is not great. The pyramids x and y were observed only with hemimorphic development, Fig. 23. The crystals were tested for pyro-electricity, but no satisfactory results were obtained, which is perhaps owing to their small size. The crystals of $CsHgBrI_2$ were about 2 mm. in diameter and had the habit shown in Fig. 24, which is quite different from that of the bromide. The forms and angles are as follows:

24.



b, 010, i-$\bar{\imath}$ $\quad$ c, 001, 0 $\quad$ l, 320, i-$\frac{3}{2}$ $\quad$ s, 034, $\frac{3}{4}$-$\bar{\imath}$

	Measured.		Measured.	Calculated.
$l \wedge l$, $320 \wedge 3\bar{2}0 =$	*66° 8′	$l \wedge s$, $320 \wedge 034 =$	*72° 22′	. . .
$b \wedge s$, $010 \wedge 034 =$	*60° 54′	$l \wedge s$, $\bar{3}20 \wedge 034 =$	76° 16′	76° 50′

The basal planes were curved and uneven, so that no satisfactory measurements could be made from them, and the other faces, although bright, did not give very satisfactory reflections. The crystals show in convergent polarized light an optical axis, almost normal to the base, the plane of the optical axes being the clinopinacoid.

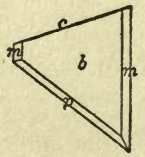
Type 2 : 3.

		$a : b : c$	
$Cs_2Hg_3I_8$	Monoclinic, hemihedral	0.3438 : 1 : 0.3544	$\beta = 71° 55\frac{1}{2}'$

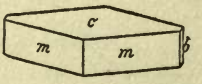
25.



26.



27.



The crystals of this salt have a curious development. Some of the most conspicuous forms are triangular plates, Fig. 25, while Fig. 26 is a projection of the same upon the

clinopinacoid. These crystals are terminated above by a basal plane and below by pyramidal faces, which gives a curious hemimorphic development in the direction of the symmetry plane. A variety of habits was observed, long prismatic, skeleton forms and simple shapes like Fig. 27, but in almost all of these the hemihedral character was prominent. The crystals frequently measured over 10 mm. in greatest diameter. The faces were bright and gave excellent reflections. The forms and angles are as follows:

b, 010, $\bar{i}$-$\bar{i}$ *c*, 001, 0 *m*, 110, *I* *p*, 11$\bar{1}$, 1

The pyramid was observed only with hemihedral development.

	Measured.		Measured.	Calculated.
$c \wedge m$, 001 ∧ 110 =	*72° 51′	$m \wedge p$, 110 ∧ 11$\bar{1}$ =	*50° 26′	. . .
$m \wedge m$, 110 ∧ 1$\bar{1}$0 =	*36° 12′	$b \wedge p$, 010 ∧ 111 =	74° 17′	74° 14′

Two cleavages were observed, one perfect parallel to the clinopinacoid, a second less perfect parallel to the base. In polarized light clinopinacoid tables give an extinction, inclined about 23° to the vertical axis in the acute angle β. Basal plates show in convergent light an optical axis not far removed from the centre of the field. The plane of the optical axes is the clinopinacoid.

These crystals furnish an excellent illustration of inclined faced hemihedrism, as recently developed by Prof. Geo. H. Williams,* who has shown that it is of frequent occurrence on pyroxene.

Type 1 : 2.

		a : *b* : *c*	
$CsHg_2Cl_5$	Monoclinic	1.6099 : 1 : 1.3289	$\beta = 78° 54'$
$CsHg_2ClBr_4$	Orthorhombic	0.586 : 1 : . . .	
$CsHg_2Br_5$	Orthorhombic	0.590 : 1 : 1.15	
$CsHg_2I_5$	Not measured.		

$CsHg_2Cl_5$ was made in slender lath-shaped crystals, over 10 mm.

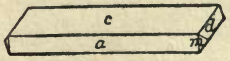


Fig. 28.

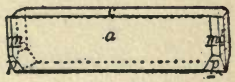


Fig. 29.

* Amer. Jour. Sci., xxxviii, 115, 1889.

long in the direction of the symmetry axis, but not over $\frac{1}{2}$ mm. in diameter. Fig. 28 represents a simple, and 29 a twin crystal, with the orthopinacoid as twinning plane. The forms and angles are as follows:

a, 100, $i\text{-}\bar{\imath}$	*c*, 001, *O*	*d*, 011, $1\text{-}\grave{\imath}$
b, 010, $i\text{-}\grave{\imath}$	*m*, 110, *I*	*p*, 111, -1

Two orthodomes were also identified, $\bar{1}01$ and $\bar{2}01$, but they were very small and yielded only approximate measurements.

	Measured.		Measured.	Calculated.
$a \wedge c$, $100 \wedge 001$	$= *78°\ 54'$	$c \wedge m$, $001 \wedge 110$	$= 84°\ 5'$	$84°\ 5'$
$a \wedge m$, $100 \wedge 110$	$= *57°\ 40'$	$m \wedge p$, $110 \wedge 111$	$= 31°\ 12'$	$31°\ 8'$
$c \wedge d$, $001 \wedge 011$	$= *52°\ 31'$	$a \wedge p$, $100 \wedge 111$	$= 58°\ 4'$	$58°\ 3'$
		$b \wedge p$, $010 \wedge 111$	$= 47°\ 19'$	$47°\ 19'$

The plane of the optical axes is at right angles to the symmetry plane, and the obtuse bisectrix is nearly normal to the base.

80.



Both $CsHg_2ClBr_4$ and $CsHg_2Br_5$ were made in rectangular tablets, Fig. 30, which were not over $1\frac{1}{2}$ mm. in greatest diameter and were very thin. Twins were common, with the unit prism as twinning plane, and the plates often penetrated at angles of about 60° and 120°, reminding one of little cerussite twins.

The forms and angles are as follows:

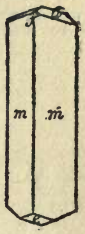
$CsHg_2ClBr_4$.	$CsHg_2Br_5$.
b, 010, $i\text{-}\check{\imath}$	*b*, 010, $i\text{-}\check{\imath}$
m, 110, *I*	*n*, 120, $i\text{-}\check{2}$
d, 011, $1\text{-}\check{\imath}$	*d*, 011, $i\text{-}\check{\imath}$
	e, 014, $\frac{1}{4}\text{-}\check{\imath}$

	Measured.	Calculated.		Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$	$= *60°\ 44'$	...	$b \wedge b$, twin	$= *61°\ 5'$	...
$b \wedge b$, twin	$= 60°\ 35'$	$60°\ 44'$	$b \wedge d$, $010 \wedge 011$	$= *41°\ 0'$	...
			$b \wedge n$, $010 \wedge 120$	$= 40°\ 20'$	$40°\ 17'$
			$b \wedge e$, $010 \wedge 014$	$= *73°\ 25'$	$73°\ 57'$

Type 1 : 5.

		a : *b* : *c*	
$CsHg_5Cl_{11}$	Monoclinic	0.7233 : 1 : 0.4675	$\beta = 85° 51' 40''$
$CsHg_5ClBr_{10}$	Monoclinic	0.7111 : 1 : 0.4561	$\beta = 85° 29'$

31.



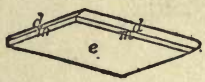
The chloride was made in prismatic crystals, fully 10 mm. long, and having the habit shown in Fig. 31. The forms and angles are as follows:

m, 110, *I* *d*, 011, 1-$\bar{\imath}$ *e*, $\bar{1}$01, 1-$\bar{\imath}$ *f*, 101, — 1-$\bar{\imath}$

The dome *f* was usually wanting.

	Measured.	Calculated.		Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$	*71° 37′	. . .	$m \wedge d$, $110 \wedge 011$	72° 31′	72° 31½′
$d \wedge d$, $011 \wedge 0\bar{1}1$	*50° 0′	. . .	$m \wedge d$, $\bar{1}10 \wedge 011$	78° 49′	78° 48′
$m \wedge e$, $\bar{1}10 \wedge \bar{1}01$	*66° 8′	. . .	$d \wedge f$, $011 \wedge 101$	39° 30′	39° 29½′
$d \wedge e$, $011 \wedge \bar{1}01$	41° 21′	41° 20½′	$e \wedge f$, $\bar{1}01 \wedge 101$	65° 43′	65° 42′

32.



The chlorobromide $CsHg_5ClBr_{10}$ is much more insoluble than the chloride and was made in crystals, which were not over ½ mm. in greatest diameter. The habit is shown in Fig. 32, and is very different from that of the chloride. The forms and angles are as follows:

m, 110, *I* *d*, 011, 1-$\bar{\imath}$ *e*, $\bar{1}$01, 1-$\bar{\imath}$

	Measured.		Measured.	Calculated.
$m \wedge m$, $110 \wedge 1\bar{1}0$	*70° 40′	$d \wedge e$, $011 \wedge \bar{1}01$	*40° 58′	. . .
$d \wedge d$, $011 \wedge 0\bar{1}1$	*48° 54′	$m \wedge d$, $110 \wedge 011$	72° 40′	72° 40′

The crystals are strongly double refracting, and the little tables show in convergent polarized light a bisectrix nearly normal to *e*. The plane of the optical axes is the clinopinacoid and the optical axial angle is small. The inference phenomena are very interesting when observed through colored glasses. In the hyperbola position the figure is almost uniaxial when viewed through red glass, while with blue the hyperbolæ are separated, probably as much as 15°–20°.

SHEFFIELD SCIENTIFIC SCHOOL,
June, 1891.

ON THE CÆSIUM- AND THE POTASSIUM-LEAD HALIDES.*

By H. L. WELLS.

As a continuation of the work on double halides, in this laboratory,† a study of the cæsium-lead salts has been undertaken by Messrs. G. F. Campbell, P. T. Walden, and A. P. Wheeler. These gentlemen have carried out the investigation with much enthusiasm and skill, and I take pleasure in expressing my obligations to them. They have established the following salts:

Cs_4PbCl_6	Cs_4PbBr_6	. . .
$CsPbCl_3$	$CsPbBr_3$‡	$CsPbI_3$
$CsPb_2Cl_5$	$CsPb_2Br_5$	. . .

These results showed the existence of three types of lead double halides, the first of which fails to conform with Remsen's law § concerning the composition of this class of bodies.

Since the recent investigations of Remsen and Herty ‖ had indicated the existence of only a single type of potassium-lead halides, a new investigation of these seemed desirable, especially since these authors had denied the existence of Boullay's salt, ¶ K_4PbI_6, which corresponds to one type of the new cæsium compounds. I have, therefore, undertaken this work, and, as a result, have obtained the following salts:

. . . . .	$K_2PbBr_4.H_2O$	. . . . .
$3KPbCl_3.H_2O$	$3KPbBr_3.H_2O$ / $KPbBr_3.H_2O$	$KPbI_3.2H_3O$
KPb_2Cl_5	KPb_2Br_5	. . . . .

* Amer. Jour. Sci., xlv, February, 1893.
† Ibid., III, xliv, 155, 157, and 221.
‡ This compound is dimorphous.
§ Amer. Chem. Jour., xi, 296.
‖ Ibid., xiv, 107.
¶ Ann. Chim. Phys., II, xxxiv, 336 (1827).

It is to be noticed that neither Boullay's iodide nor any corresponding chloride or bromide was obtained among these salts. On the other hand, the compound $K_2PbBr_4.H_2O$ belongs to a type which had not been discovered among the cæsium salts, so that, taking the cæsium and potassium series together, the existence of four types of double lead halides is shown.

The compound K_2PbBr_4, the anhydrous form of the salt just mentioned, is ascribed to Löwig,* but although iodides belonging to the same type have been described, $K_2PbI_4.4H_2O$ by Ditte † and $K_2PbI_4.2H_2O$ by Berthelot, ‡ neither Remsen and Herty nor I have been able to prepare them. Although these iodides and Boullay's salt, K_4PbI_6, belong to types which certainly exist, I am inclined to believe, with Remsen and Herty, that the products which gave these formulæ were mixtures of $KPbI_3.2H_2O$ and KI. The absence of more than one iodide in the cæsium series strengthens this view.

Remsen and Herty obtained the salt $KPbI_3.2H_2O$ under wide variations of conditions, and I have confirmed their results. This salt was first obtained by Boullay § and analyzed by him, after drying over lime, in an anhydrous condition. Berthelot ‖ has described a compound, $K_4Pb_3I_{10}.6H_2O$, which differs but slightly in required composition from the above salt, and his description of it agrees with that compound. There is no doubt, therefore, that he really obtained the compound $KPbI_3.2H_2O$ and that his analyzed products were slightly contaminated with potassium iodide. Berthelot attributes $K_4Pb_3I_{10}$ to Boullay. The latter chemist, however, derived the correct formula, equivalent to $KPbI_3$, from his analysis, but since this did not agree closely with theory, Gmelin ¶ derived the above-mentioned formula from it, and this has been frequently copied in more recent chemical literature.

* Gmelin's Handbook, English ed. of 1850, v. 162.
† Ann. Chim. Phys., V, xxiv, 226, 1881.
‡ Ibid., xxix, 289, 1883.
§ Ibid., II, xxxiv, 336, 1827.
‖ Ibid., V, xxix, 289, 1883.
¶ Handbook, English ed., 1850, v, 161.

Schreinemakers,* in connection with an investigation on the equilibrium of the double salt of iodide of lead and potassium in aqueous solution, has assumed that Ditte's formula was correct as far as the composition of the anhydrous compound was concerned. By making a number of water determinations, without determining lead, potassium, or iodine, he arrived at the formula $K_2PbI_4.2\frac{1}{2}H_2O$. It is absolutely certain, from his description of the salt and his method of preparing it, that he had the compound $KPbI_3.2H_2O$; moreover, his water determinations, 5.52, 5.72, 5.89, 5.93, and 5.16 per cent, agree satisfactorily with the calculated amount, 5.90, for this salt.

Remsen and Herty made only a single chloride, and likewise only one bromide. The other chloride, and the two bromides belonging to other types crystallize beautifully and are as easily made as the salts which they prepared, and it is a strange coincidence that the latter happened to correspond in type to the iodide which they had obtained. I have confirmed the composition of their bromide, $KPbBr_3.H_2O$, but their chloride, to which they gave the formula $KPbCl_2$ is evidently identical with the compound which I have found to be undoubtedly hydrous, $3KPbCl_2.H_2O$.

Löwig, as already mentioned, has described the compound K_2PbBr_4. I have been unable to find his original article, but from the fact that I have not obtained an anhydrous form of this compound, I believe that he overlooked the water of crystallization or dehydrated the salt before analyzing it.

A bromide, $K_2Pb_3Br_8$ is mentioned by Berthelot.† He does not give any analysis or description of it, and I am convinced from my own experiments that he obtained a mixture of $KPbBr_3.\frac{1}{3}H_2O$ and KPb_2Br_5.

Strohecker ‡ states that he produced three different chlorides of potassium and lead by mixing potassium chloride and lead nitrate solutions. It is remarkable, considering the abundance

* Zeitschr. Physikal. Chem., ix, 57, 1892.
† Ann. Chim. Phys., V, xxix, 289, 1883.
‡ Jahresbericht, 1869, 282.

and cheapness of the materials and the ease with which large quantities of the double salts can be made, that he did not obtain them in sufficient quantities for exact analyses. Since I have succeeded in making only two double chlorides, I believe that one of Strohecker's salts, which he describes as feathery, was simply lead chloride.

The results of previous investigators may be summed up by saying that it is probable that no potassium-lead halides have been correctly described, if water of crystallization is taken into consideration, except two of Remsen and Herty's salts, $KPbBr_3.H_2O$ and $KPbI_3.3H_2O$.

Method of Preparation.

Both the cæsium and potassium salts have been investigated, in every case, by making hot, aqueous solutions of the component halides and cooling to crystallization. Some previous investigators had used solutions of lead nitrate and an alkaline halide for the purpose, but their example has not been followed, because it was not believed that the presence of an alkaline nitrate would in any way facilitate the operation, and it was feared that it might incur contamination in some cases. The conditions were gradually varied from a point where the alkaline halide crystallized out, to a point where the lead halide was deposited uncombined, and the experiments were so carefully carried out and so frequently repeated that it seems scarcely possible that any double salt was overlooked.

The salts have been made on a rather large scale. In the case of the cæsium compounds, the rarity of the material made it necessary to perform the separate experiments with only about 50 or 75 g. of a cæsium halide, but in making the potassium salts 400 or 500 g. of a potassium halide were frequently used.

Solutions which were neutral or slightly acid were generally used. The effect of the presence of a large amount of free acid, hydrochloric, hydrobromic, or hydroiodic, as the case required, was also carefully studied, but these had no apparent effect upon the results.

Very large crops of the potassium salts were sometimes formed, so that the homogeneity of the mass was doubtful. In such cases the greater part of the crop was removed and satisfactory crystals were obtained by dissolving the remainder in the mother-liquor by the aid of heat and cooling.

The cæsium material used was wholly from the pollucite of Hebron, Maine.* The salts were carefully purified for this investigation. Godeffroy's method† was found to be very satisfactory for the purpose of separating cæsium from the sodium and potassium which accompany it in the mineral.

Kahlbaum's potassium chloride, bromide, and iodide were usually used for making the potassium salts, but for a few experiments the ordinary medicinal potassium bromide was substituted. Since some of the analyses of the double bromide show an excess over 100 per cent, it is suspected that the salts contained a little chlorine. Calculation shows that one per cent of chlorine replacing bromine would cause an excess of 0.71 per cent if the chlorine was weighed as silver chloride and calculated as bromine.

The lead halides which were used were prepared by ourselves from reliable materials.

General Properties.

The lead double halides are all decomposed by water, and the presence of a large excess of the alkaline halide is necessary for the formation of all the compounds to be described except $CsPb_2Cl_5$ and $CsPb_2Br_5$, which are almost stable with water. The concentration of the alkaline halide solution evidently determines, in the cases of the chlorides and bromides, the type of salt produced. Since the simple cæsium halides are much more soluble than those of potassium, it is possible to use them in much more concentrated solutions, and the salts of Cs_4PbCl_6 and Cs_4PbBr_6 are readily obtained. In the case of potassium bromide the solution becomes saturated with the simple salt by concentration just beyond the

* Amer. Jour. Sci., III, xli, 213. † Berichte d. Chem. Ges., vii, 375.

point where $K_2PbBr_4.H_2O$ is obtained, and with potassium chloride, which is less soluble than the bromide, the limit is reached at the compound $3KPbCl_3.H_2O$. The apparent existence of only a single double iodide, both with cæsium and potassium, is remarkable, since cæsium iodide is very soluble and potassium iodide is much more soluble than the bromide and chloride.

On account of their decomposition by water, no determinations of the solubility of the double halides have been made, but it was noticed that the cæsium compounds were much less soluble in the saline solutions than the corresponding potassium salts. This relation corresponds with the observation of Godeffroy,* that while the simple salts increase in solubility from potassium to cæsium, the double and complicated salts show a decrease in this direction.

All the chlorides and bromides described in this article are colorless, or in one case nearly so except two cæsium salts, $CsPbCl_3$ and one modification of $CsPbBr_3$. The first of these is pale yellow and the other bright orange. These colors are very remarkable since the simple halides from which they are made are all colorless. I have previously observed a similar case, where a colored double halide was formed from two colorless halides, in the compound $CsHgBr_3$. † Both double iodides are yellow, the hydrous potassium salt being the paler of the two.

Analytical Methods.

Great care was used in selecting homogeneous material for analysis. The crystals were dried as rapidly and thoroughly as possible by pressing them between smooth filter-papers, and where the substance did not lose its lustre by the operation, it was then exposed to the air for several hours.

Water was determined by collecting and weighing it in a calcium-chloride tube, the substance being ignited in a combustion-tube, behind a layer of dry sodium carbonate, in a

* Berichte d. Chem. Ges., ix, 1365. † Amer. Jour. Sci., III, xliv, 227.

current of dry air. The water lost over sulphuric acid or at certain temperatures was determined by the usual methods.

Lead was determined in two ways. With all the cæsium salts the substance was dissolved in hot water (an easy operation with all these salts, but impracticable in the case of some of the potassium compounds), and all except a trace of lead was precipitated by ammonium carbonate in presence of ammonium hydroxide. The precipitate of lead carbonate was removed by filtration, and the remaining trace of lead was precipitated by passing hydrogen sulphide into the alkaline solution. The lead sulphide was collected and ignited by itself in a porcelain crucible. The amount of this was so small that it was evident that no appreciable error would arise from any lead sulphate that the ignited residue might contain, so that the main precipitate of lead carbonate was ignited in the same crucible and the whole was weighed and calculated as lead oxide. A different method was selected for the determination of lead in the potassium compounds, for the reason that some of them could not be readily dissolved in hot water, and it was found to be more convenient and expeditious than the other. About 1 g. of substance was dissolved in about 10 c. c. nitric acid (sp. gr. 1.20), about 2 c. c. concentrated sulphuric acid, previously diluted with water, were then added, and the nitric acid was removed by evaporation. After diluting with about 25 c. c. of water and cooling, the lead sulphate was collected in a Gooch crucible, washed with very dilute sulphuric acid, ignited, and weighed.

In order to determine cæsium, the alkaline solution from which the lead had been removed was concentrated until the ammonium carbonate, hydroxide, and sulphide had been nearly or quite removed, a small excess of sulphuric acid was added, and, after evaporation and ignition, normal cæsium sulphate was obtained by igniting in a current of air containing ammonia, and this was weighed.

The filtrates from the lead sulphate did not contain an appreciable amount of lead. Normal potassium sulphate was obtained from these solutions by evaporating, igniting, and heating in an ammoniacal atmosphere.

The halogens were determined as silver halides. Where the substance could be completely dissolved in hot water, an excess of silver nitrate was added to the hot solution and it was afterwards acidified with nitric acid. When it happened that the lead halide remained partly undissolved, the nitric acid was not added until this had been completely decomposed by long digestion on the water-bath with an excess of silver nitrate. The precipitates were collected and weighed in Gooch crucibles.

The Cæsium-Lead Chlorides.

By G. F. CAMPBELL.

Cs_4PbCl_6. — When lead chloride is dissolved, by the aid of heat, in a solution of cæsium chloride which is so concentrated as to be nearly saturated when cold, this salt is deposited on cooling in the form of brilliant white rhombohedrons. Crystals having a diameter of 2 or 3 mm. were sometimes obtained. Two entirely separate crops were analyzed, both of which were undoubtedly free from other compounds.

	Found.		Calculated for Cs_4PbCl_6.
Cæsium	55.60	56.03	55.90
Lead		21.63	21.75
Chlorine	21.97	22.23	22.35
		99.89	100.00

$CsPbCl_3$. — On gradually diluting the concentrated solution of cæsium chloride, such as was used in making the previous salt, and dissolving lead chloride in it as before, a point is soon reached where short prismatic crystals of small size and of a pale yellow color are deposited on cooling. Three different crops of apparently pure crystals were analyzed.

	Found.			Calculated for $CsPbCl_3$.
Cæsium . . .	31.33	30.54	30.13	29.79
Lead	44.99	45.28	46.29	46.36
Chlorine . . .	23.85	23.75	23.71	23.85
	100.17	99.57	100.13	100.00

$CsPb_2Cl_5$. — Experiments with still more dilute solutions, carried out in a similar manner, gave, under wide variations of conditions, this salt in the form of thin white plates which were often several millimeters in diameter. These plates presented marked variations in habit, which were apparently due to changes in the conditions under which they were made. In two crops, of which A and B are the analyses, the plates were uniformly rhomboidal in form. Two other crops, C and D, were made up of lengthened plates, so twinned as to form feathery aggregates. In another crop, E, made from a more dilute solution than the others, the plates were apparently square.

	Found.					Calculated for $CsPb_2Cl_5$.
	A.	B.	C.	D.	E.	
Cæsium . .	19.99	18.44	18.27	. . .	18.45	18.36
Lead . . .	57.14	57.16	57.06	56.98	57.08	57.16
Chlorine . .	. . .	24.47	. . .	24.52	24.35	24.48
		100.07			99.88	100.00

The three different habits in which this salt crystallizes are so distinct in appearance that, before the samples were analyzed, it was supposed that they were separate compounds. It appears probable that the compound is at least dimorphous.

The Cæsium-Lead Bromides.

By P. T. WALDEN.

Cs_4PbBr_6. — This salt is produced, in concentrated solutions, similarly to the corresponding chloride. Like the latter salt, it forms white rhombohedrons. The crystals were usually not over 1 or 2 mm. in diameter. Two separate crops were prepared and analyzed.

	Found.		Calculated for Cs_4PbBr_6.
Cæsium	43.61	43.42	43.64
Lead	16.83	16.83	16.98
Bromine . . .	39.24	39.33	39.38
	99.68	99.58	100.00

$CsPbBr_3$. — This compound is dimorphous. One modification forms small prisms of a bright orange color, the other is

pure white and crystallizes in slender needles. The orange salt is obtained when lead bromide is dissolved in somewhat more dilute solutions of cæsium bromide than those required for the formation of Cs_4PbBr_6, and there is a narrow range of conditions where it crystallizes upon the latter salt. There is, therefore, no evidence of the existence of an intermediate compound, Cs_2PbBr_4, corresponding to one of the potassium-lead bromides. Whenever solid lead bromide is added to a concentrated solution of cæsium bromide, it instantly loses its white color and takes on that of the orange salt. The white needles are formed in solutions which are slightly more dilute than those required for the orange modification. The limits of the conditions under which this white salt is formed are very narrow, and a great many trials were necessary before satisfactory crops were obtained. Two distinct samples of each salt were analyzed. The white needles were not absolutely free from the orange compound, but there is no doubt that they were sufficiently pure to show their composition accurately.

	Found.				Calculated for $CsPbBr_3$.
	Orange Salt.		White Salt.		
Cæsium . . .	23.19	23.13	23.02	22.49	22.93
Lead	35.69	35.39	35.24	35.88	35.69
Bromine . . .	41.37	41.34	41.47	41.45	41.38
	100.25	99.86	99.73	99.82	100.00

On heating the white modification to about 140°, it gradually assumes the exact color of the orange salt, without changing its external form, and this color is permanent on cooling.

$CsPb_2Br_5$. — This salt is produced in solutions which are still more dilute than those from which the preceding compounds are obtained. It was first noticed at a volume of about 160 c. c. of a solution containing about 50 g. of cæsium bromide. It continued to form, on further dilution and the addition of lead bromide, until the volume reached 1250 c. c., when lead bromide began to be deposited. The conditions under which the salt is formed are, therefore, very wide. The compound crystallizes in thin white plates, which, like

the corresponding chloride, present considerable differences in habit. Plates having a diameter about 5 mm. were sometimes obtained. Three separate crops of crystals were analyzed.

	Found.			Calculated for $CsPb_2Br_5$.
Cæsium . .	14.13	14.35	. . .	14.05
Lead . . .	43.39	43.72	43.45	43.71
Bromine . .	42.23	42.21	. . .	42.24
	99.75	100.28		100.00

The Cæsium-Lead Iodide and some Mixed Double Halides.

By A. P. WHEELER.

$CsPbI_3$. — Under a great variety of conditions this was the only double iodide that could be produced. The compound is but slightly soluble in hot cæsium-iodide solutions, so that the crops obtained were always small. It forms very slender rectangular prisms which are yellow in color. The following analyses were made on separate products:

	Found.		Calculated for $CsPbI_3$.
Cæsium	17.90	. . .	18.45
Lead	28.38	27.40	28.71
Iodine	52.83	52.57	52.84
	99.11		100.00

Three double salts have been made by dissolving lead bromide in solutions of cæsium chloride. The analyses show that the two salts do not combine unchanged, but that there is usually an extensive exchange of halogens. Each of the products must be considered, therefore, as a mixture of a double chloride with the corresponding double bromide.

$Cs_4Pb(Cl, Br)_6$. — This was produced in rhombohedrons, like the chloride and bromide. Two crops were analyzed.

	Found.	
Cæsium	54.65	55.50
Lead	19.30	18.61
Chlorine	15.89	19.90
Bromine	9.52	4.03
	99.36	98.04
Ratio Br : Cl . . .	1 : 3.8	1 : 11.2

$CsPb(Cl, Br)_3$. — This occurred in small rectangular prisms, like the chloride and bromide and having a yellow color intermediate between them. Two crops gave the following analyses:

	Found.	
Cæsium	30.24	30.50
Lead	44.23	43.55
Chlorine	21.44	18.94
Bromine	4.00	8.79
	99.91	101.96
Ratio Br : Cl . . .	1 : 12	1 : 4.8

$CsPb_2(Cl, Br)_5$. — This was obtained in white plates resembling the two double salts. Two products were analyzed.

	Found.	
Cæsium	18.94	. . .
Lead	51.40	51.97
Chlorine	16.29	19.31
Bromine	13.27	8.62
	99.90	
Ratio Br : Cl . . .	1 : 2.8	1 : 5

The Potassium–Lead Halides.

In studying these bodies care has been taken to record the conditions under which they were made. These conditions in many cases are only approximately given, because uncertain quantities of salts had often been removed from the solutions, either for analysis or in order to obtain smaller and better crops of crystals. A large number of analyses have been

made in some cases. This was due to the fact that the salts often varied so little in appearance that it was necessary to analyze many products in order to identify them and to be certain that they were not different compounds.

$3KPbCl_3.H_2O$. — When lead chloride is dissolved in a hot solution of potassium chloride which is so concentrated as to be nearly saturated when cold, this double salt is deposited on cooling. It forms brilliant prismatic crystals which are largest in the most concentrated potassium-chloride solutions. The largest crystals obtained had a length of more than 10 mm. and a diameter of 1 or 2 mm. It was noticed that, when sufficiently concentrated solutions were used, pure potassium chloride crystallized upon this compound, and no evidence was obtained of the existence of a double salt containing a larger proportion of potassium chloride than this.

The following table gives the approximate conditions under which the five samples which were analyzed were made:

	KCl. g.	$PbCl_2$. g.	Volume. c. c.	Volume for 1 g. KCl. c. c.
A	400	30	1100	$2\frac{3}{4}$
B	400	80	1200	3
C	150	40	450	3
D	100	25	350	$3\frac{1}{2}$
E	300	55	1300	$4\frac{1}{3}$

The results of the analyses are as follows:

	Found.					Calculated for $3KPbCl_3.H_2O$.
	A.	B.	C.	D.	E.	
K . . .	11.38	11.10	10.79	. . .	. . .	10.90
Pb . .	57.46	57.68	57.43	57.94	57.14	57.73
Cl . . .	29.91	29.87	29.81	. . .	. . .	29.70
H_2O . .	1.45	1.39	. . .	1.51	1.88	1.67
	100.20	100.04				100.00

All the samples were thoroughly air-dried before they were analyzed. By this treatment the crystals did not lose any of their lustre. A finely pulverized portion of sample A lost only 0.02 per cent in weight after standing over concentrated

sulphuric acid for eight days. The same sample suffered an additional loss of 0.23 per cent when heated for twelve hours in a steam drying-oven. The water was not rapidly given off until a temperature of about 200° was reached. The salt decrepitates when heated rapidly to about 200°, corresponding in this respect to the salt which Remsen and Herty described as anhydrous and to which they gave the formula $KPbCl_3$. There can be no doubt, therefore, that Remsen and Herty's formula is incorrect.

KPb_2Cl_5. — This salt is formed in more dilute solutions than those which produce the previously described compound. It occurs, like that compound, in white prismatic crystals, but it differs considerably from it in lustre and form, so that the two salts can be distinguished by microscopic examination. The salt under consideration is anhydrous, and this fact makes it easy to distinguish this compound, when pure, from the other.

Four analyzed crops were made under the following conditions:

	KCl.	$PbCl_2$.	Volume.	Volume for 1 g. KCl.
	g.	g.	c. c.	c. c.
A	200	50	1500	$7\frac{1}{2}$
B	150	30	1100	$7\frac{1}{3}$
C	150	20	1100	$7\frac{1}{3}$
D	250	55	1200	$4\frac{8}{10}$

The analyses were as follows:

	Found.				Calculated for KPb_2Cl_5.
	A.	B.	C.	D.	
Potassium . . .	6.14	5.97	6.18	6.07	6.20
Lead	64.74	66.43	65.85	65.72	65.65
Chlorine . . .	28.11	. . .	28.13	28.08	28.15
Water	0.11	. . .	. . .	. . .	0.00
	99.10		100.16	99.87	100.00

There was no indication of the formation of any other double chloride, as the dilution was increased beyond that given for the above products, and when a solution containing 1 g. of KCl in 11 c. c. was used pure lead chloride was deposited.

$K_2PbBr_4.H_2O$. — This salt is obtained by dissolving lead

bromide in the most concentrated solutions of potassium bromide. It forms brilliant prismatic crystals which are permanent in the air. The largest of these which were obtained were about 1 mm. in diameter and 5 mm. in length. A number of crops were made under the following conditions:

	KBr.	$PbBr_2$.	Volume.	Volume for 1 g. KBr.
	g.	g.	c. c.	
A	400	70	700	$1\frac{3}{4}$
B	400	90	700	$1\frac{3}{4}$
C	400	120	800	2
D	400	130	650	$1\frac{6}{10}$
E	500	130	850	$1\frac{7}{10}$
F	500	130	775	$1\frac{6}{10}$

These products gave the following analyses:

	K.	Pb.	Br.	H_2O.	
A	12.51	34.25	51.47	2.50	= 100.73
B	12.21	34.59	51.21	2.51	= 100.52
C	11.89	34.47	51.14	2.44	= 99.94
D	12.37	34.50	51.35	. . .	
E	. . .	34.26	51.40	2.61	
F	12.70	33.89	51.46	2.57	= 100.62
Calculated for $K_2PbBr_4.H_2O$	12.55	33.21	51.35	2.89	= 100.00

This salt is apparently stable in the air, but it loses water very slowly over sulphuric acid. A finely powdered sample of A lost 0.23 per cent after remaining twelve hours in the desiccator, and the same portion suffered an additional loss 0.33 after eight days. A sample which was not pulverized lost only 0.09 per cent in twelve hours and, in addition, 0.17 per cent in eight days. About one-half of the water went off when the substance was heated for twelve hours in a steam drying-oven. At 200° the water is rapidly and completely expelled.

$3KPbBr_3.H_2O$. — The conditions under which this salt can be made are rather narrow, and these conditions encroach upon those of the preceding compound, so that small differences in the amounts of lead chloride used or in the temperature of the solution are sufficient to cause the formation of the other

salt. It forms brilliant, colorless, lozenge-shaped crystals which can be easily distinguished from the other compound. The crystals which were obtained sometimes had a diameter of 2 or 3 mm.

The crops analyzed were made under the following conditions:

	KBr. g.	$PbBr_2$. g.	Volume. c. c.	Volume for 1 g. KBr.
A . . .	500	130	950	$1\frac{9}{10}$
B . . .	500	130	1050	$2\frac{1}{10}$
C . . .	500	140	900	$1\frac{8}{10}$
D . . .	500	120	1050	$2\frac{1}{10}$
E . . .	500	120	1125	$2\frac{1}{4}$

The analyses were as follows:

	K.	Pb.	Br.	H_2O.
A	8.44	41.91	. . .	1.29 . . .
B	8.02	42.71	48.95	1.62 = 101.30
C	8.60	41.61	49.16	1.60 = 100.97
D	8.08	42.69	48.91	1.14 = 100.82
E		42.61	. . .	1.17 . . .
Calculated for $3KPbBr_3.H_2O$	7.95	42.06	48.77	1.22 = 100.00

The salt is stable in the air. A sample, after standing seven days over sulphuric acid, lost only 0.04 per cent. The water is given off very slowly at 100°.

$KPbBr_3.H_2O$. — This salt was described by Remsen and Herty. At summer temperature, about 25°, I was unable to obtain it, but by placing the mother-liquors from the preceding salt in an ice-chest, beautifully crystallized crops of it were obtained.

Its formation was also noticed at laboratory temperatures when the weather was somewhat cooler than in midsummer. It forms prismatic crystals. Some of those obtained were about 10 mm. long and 2 mm. in diameter. Two crops were analyzed.

	Found.		Calculated for $KPbBr_3.H_2O$.
Potassium	8.24	7.90	7.76
Lead	41.23	41.20	41.06
Bromine	47.81	. . .	47.61
Water	3.28	3.64	3.57
	100.56		100.00

The salt is usually permanent in the air, but in dry weather the crystals gradually become opaque, and over sulphuric acid about two-thirds of the water is rapidly given off.

KPb_2Br_5. — This salt crystallizes in square plates, sometimes 3 or 4 mm. in diameter. It can be readily distinguished from the other double bromides, not only by its form, but from the fact that it quickly assumes a pale green color when exposed to daylight. On long exposure, or in direct sunlight, this color changes to a pale dirty-brown. I have observed that lead bromide itself becomes nearly black on long exposure to daylight. This fact does not appear to be generally known.

The samples analyzed were made under the following conditions:

	KBr. g.	$PbBr_2$. g.	Volume. c. c.	Volume for 1 g. KBr.
A	400	130	1050	$2\frac{2}{5}$
B	400	150	1250	$3\frac{1}{8}$
C	200	75	1000	5

The results of the analyses are as follows:

	Found.			Calculated for KPb_2Br_5.
	A.	B.	C.	
Potassium . .	4.75	4.75	4.71	4.58
Lead	49.22	49.11	48.48	48.53
Bromine . . .	47.03	46.98	46.89	46.89
	101.00	100.84	100.08	100.00

$KPbI_3.2H_2O$. — It has already been mentioned that this is the only double iodide that either Remsen and Herty or I have been able to make. It forms slender, pale yellow needles, and is produced under a great variety of conditions. Two samples were analyzed. A was made with about 450 g. KI,

75 g. PbI_2, and 600 c. c. volume. For B about 400 g. KI, 45 g. PbI_2, and 280 c. c. volume were used.

	Found. A.	Found. B.	Calculated for $KPbI_3.2H_2O$.
Potassium	6.03	6.07	5.90
Lead	30.73	30.13	31.21
Iodine	57.57	56.99	57.46
Water	5.26	6.04	5.43
	99.59	99.23	100.00

The salt is apparently stable in the air, but it loses water in the desiccator.

SHEFFIELD SCIENTIFIC SCHOOL,
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ON THE DOUBLE HALIDES OF TELLURIUM WITH POTASSIUM, RUBIDIUM, AND CÆSIUM.*

By H. L. WHEELER.

THE existence of double halides of tellurium with potassium, sodium, and ammonium was first indicated by Berzelius.† He described the methods by which he obtained them, but gave no analyses of the compounds. Later, Rammelsberg ‡ investigated the double chlorides of tellurium with potassium and ammonium, with the object of determining their composition. He arrived at the formulæ $8KCl.3TeCl_4$ and $8NH_4Cl.3TeCl_4$. It will be shown beyond that the formula of the potassium compound at least must have been obtained from analyses of impure products. Von Hauer § analyzed the double bromide of tellurium and potassium, and concluded that the salt had the composition represented by the formula $2KBr.TeBr_4.3H_2O$. I have reinvestigated this salt and found it to contain two molecules of water and not three. Probably Von Hauer analyzed the salt without previously having dried it sufficiently or without having taken precautions to remove included water which the crystals always contain. He dehydrated this salt and used it in his work on the atomic weight of tellurium.

More recently Wills ‖ determined the atomic weight of tellurium by means of the same salt. He does not give any analyses of the hydrous compound, but states that the salt contains water and gives directions for dehydrating it. Rammelsberg in his "Handbuch der krystallographisch-physikalischen Chemie" (p. 289) quotes the formula of the

* Amer. Jour. Sci., xlv, April, 1893.
† Pogg. Ann., xxxii, 577.
‡ Berlin Monats. Ber., 1875, 379.
§ J. prakt. Chem., lxxiii, 98.
‖ Jour. Chem. Soc., xxxv, 711.

dehydrated compound from Wills's work and assigns to this Baker's * measurements, which do not belong to it, but to the hydrated compound with the three supposed molecules of water of crystallization. The present investigation has shown that the anhydrous salt is isometric, the hydrous one being orthorhombic.

Ramsay † says that "By mixing aqueous solutions of the constituent halides, tellurium halides combine thus: $TeCl_4 2KCl$, $TeBr_4.2KBr$, $TeI_4.2KI$. These compounds form reddish crystals. Few attempts have been made to prepare double halides." Although a thorough search of the literature on this subject has been made, in connection with the present work, no analyses of the double chloride or iodide could be found. Berzelius's work as regards their preparation and Rammelsberg's attempt to determine the formula of the chloride comprise all the work that has been done on these two salts. It must be concluded that the formulæ given by Ramsay were deduced by analogy with the double bromide, especially since his statements in regard to color, method of preparation and composition only apply, in all respects, to the double bromide.

It will be seen from the above summary that very little satisfactory work has been done on this class of compounds, and therefore the present investigation has been undertaken with the view of making a thorough study of the double halides of tellurium with potassium, rubidium, and cæsium. As a result the following compounds have been prepared:

$2KCl.TeCl_4$	$2RbCl.TeCl_4$	$2CsCl.TeCl_4$
$2KBr.TeBr_4$	$2RbBr.TeBr_4$	$2CsBr.TeBr_4$
$2KBr.TeBr_4.2H_2O$	$2RbI.TeI_4$	$2CsI.TeI_4$
$2KI.TeI_4.2H_2O$	. . . . .	. . . . .

It is to be noticed that all of these compounds conform to the usual type of double halides of tetravalent metals in con-

* Jour. Chem. Soc., xxxv, 711.

† System of Inorganic Chemistry, edition of 1891, p. 168.

taining the alkali metal and tellurium in the ratio of two atoms of the former to one of the latter, and no indications of the formation of salts of a different type were observed. The anhydrous double halides of tellurium crystallize in the isometric system with an octahedral habit, and it is an interesting fact that this form seems to be characteristic for anhydrous double halides of this type. The cæsium and rubidium salts are new compounds, as well as the crystallized, anhydrous, double potassium bromide. New formulæ have been assigned to the hydrous potassium double bromide and to the double iodide of potassium. A considerable difference is shown in the affinity of the double halides of tellurium and potassium for water of crystallization. The double chloride is anhydrous and no hydrous form of it was observed, the double bromide was prepared in both the hydrous and the anhydrous forms, while the iodide was obtained only with water of crystallization. This water was more firmly held than in the case of the hydrous bromide, as was shown by the fact that it formed from hot solutions and did not as readily effloresce.

The methods used in the preparation of pure material for this work, and which deserve to be mentioned on account of giving satisfactory results, are given below. The tellurium was obtained by purifying the commercial product by precipitation with sulphurous acid, according to the method of Divers and Shimosé.* The halides of tellurium were prepared from this material in the usual way.

Cæsium chloride was obtained in a pure state by the method of Godeffroy.† The bromides and iodides were obtained in the usual manner from the carbonate, the latter having been prepared from the pure chloride by converting into nitrate, then into oxalate and igniting the latter, as suggested by J. L. Smith,‡ for the conversion of potassium chloride into carbonate. The rubidium was purified by Allen's § acid tartrate method. In the case of the potassium salts, Kahlbaum's pure material was used.

* Jour. Chem. Soc., xlvii, 439.

† Ber. d. chem. Ges., vii, 375.

‡ Amer. Jour. Sci., II, xvi, 373.

§ Ibid., xxxiv, 367.

The methods by which the double halides were obtained will be given with the description of the salts.

Method of Analysis.

The anhydrous salts were removed from the mother-liquor, and, after pressing on filter paper, were dried in the air. The hydrous compounds were rapidly crushed on smooth filter paper, and, as soon as it was certain that no included water was retained by the fragments, they were placed in weighing tubes. Portions of about half a gram were taken for analysis. In order to determine the halogens, silver sulphate was added to the solution of the weighed sample in water containing a little sulphuric acid. The silver halide was washed, ignited, and weighed in the usual manner. After the removal of the excess of silver by means of hydrochloric acid, tellurium was removed with hydrogen sulphide. This separation of tellurium, best in warm solution, has been found to be complete in a few minutes and in a condition that admits of filtration without inconvenience. The sulphide of tellurium, filtered on asbestos in a Gooch crucible, was washed with water containing a little hydrogen sulphide, then treated with a solution of bromine in dilute hydrochloric acid, which readily dissolves the moist sulphide. An excess of nitric acid was then added to this solution and the whole evaporated on the water bath; the resulting tellurous acid, being transferred to platinum, was ignited and weighed as TeO_2. The alkali metals were determined by evaporating the filtrate from the tellurium sulphide to dryness, with an excess of sulphuric acid. The residues were then converted into normal sulphate by ignition in a stream of ammonia, as suggested by Krüss for potassium sulphate. In the case of the hydrous salts, water was determined by heating them in an air bath to constant weight; the residues were analyzed and found to correspond in composition to the anhydrous salts. The atomic weights used in the calculation of the results were the following:

Te, 125; K, 39.1; Rb, 85.5; Cs, 133; Cl, 35.5; Br, 80; I, 127.

Solubility.

The salts are all decomposed by water. The double bromides, however, show an interesting difference in their deportment with this reagent. Potassium tellurium bromide dissolves in a small amount of water, but, if an excess of water is added, tellurous acid separates, as has been observed by Wills.* Rubidium tellurium bromide also dissolves in a little hot water completely, the difference being shown on cooling, when a considerable portion of the tellurium separates as tellurous acid. In the case of the cæsium salt both hot and cold water, in large and small amounts, fail to dissolve the salt, the result being immediate decomposition. Only a small part of the tellurium in this case goes into solution. Most of these double salts can be conveniently recrystallized from dilute solutions of the corresponding acid. The exceptions are potassium-tellurium chloride, which is decomposed by this treatment, and cæsium-tellurium iodide, which is practically insoluble in hydriodic acid. The fact, first noticed by Godeffroy,† that double halides, containing the metals potassium, rubidium, and cæsium, generally decrease in solubility from potassium to cæsium, which has frequently been noticed in this laboratory, is again well illustrated by these compounds. For the determination of the solubility of these salts in acids, they were finely powdered, and saturated solutions were then prepared by digesting a mixture of the acid and an excess of the salt for about a week, at ordinary temperature. This was done in a closed flask. Weighed portions of these solutions were evaporated to dryness and the residues dried at 100° and weighed. These solubilities were all taken at 22°, and the results are the average of two or more closely agreeing determinations.

	100 parts HCl Sp. gr. 1.2 dissolve	100 parts HCl Sp. gr. 1.05 dissolve
$2RbCl.TeCl_4$ . . .	0.34 parts	13.09 parts
$2CsCl.TeCl_4$ . . .	0.05 "	0.78 "

* Loc. cit.

† Ber. d. Chem. Ges., viii, 9.

	100 parts HBr Sp. gr. 1.49 dissolve	100 parts HBr Sp. gr. 1.08 dissolve
$2KBr.TeBr_4$ . . .	6.57 parts	62.90 parts
$2RbBr.TeBr_4$ . . .	0.25 "	3.88 "
$2CsBr.TeBr_4$ . . .	0.02 "	0.13 "

The double tellurium chlorides, described in this article, are more soluble than the bromides, and the bromides more soluble than the iodides. The solubility of these compounds in strong alcohol shows the same gradation as their solubility in acids, the cæsium salts being practically insoluble in this menstruum, while the rubidium salts dissolve to a trifling but clearly perceptible extent, and the potassium salts dissolve considerably or are decomposed with separation of the potassium halide, or both solution and decomposition take place, according to the salt experimented with.

The Chlorides.

The crystals of the three chlorides have a pale yellow color, resembling that of the well-known ammonium phosphomolybdate precipitate, the shade becoming somewhat lighter from the cæsium to the potassium salts.

Cæsium Tellurichloride, $2CsCl.TeCl_4$. — In the preparation of this compound, and also in the preparation of the rubidium and potassium double chlorides, the tellurium tetrachloride is most conveniently made by converting tellurium into tellurous oxide by means of aqua regia, evaporating to dryness to expel nitric acid and then dissolving the residue in hot hydrochloric acid. An aqueous solution of cæsium chloride, added to this, produces a precipitate, even in quite dilute solutions. There must be an excess of hydrochloric acid present to prevent the separation of tellurous acid. On boiling and adding more water, if necessary, this precipitate dissolves. The solution, left to cool, deposits small brilliantly lustrous octahedra. It is a general fact, with these double halides, that an excess of one or the other of the constituents does not affect their composition. This is shown in this particular case by the fact that it can be recrystallized from strong solutions of tellurium or of cæsium chlorides.

	Analysis gave			Calculated.
Cs	43.44	43.90	44.63	44.04
Te	20.65	. . .	21.41	20.69
Cl	35.93	35.14	. . .	35.27

This compound is perfectly stable in the air. It does not melt below the boiling-point of sulphuric acid. It can be precipitated from its solution in dilute hydrochloric acid by the addition of concentrated hydrochloric acid. A portion of the salt, finely pulverized, was treated with water at ordinary temperature. This produced a voluminous white precipitate, which was washed with cold water and dried in the air.

	Analysis gave	Calculated for H_2TeO_3.
Te	71.43	71.43
H_2O	7.52	10.29
O	17.76	18.28
Cl	2.49	. . .
Cs	0.80	. . .

The oxygen which was not given off in the form of water on heating the substance was calculated by difference. From the above analysis the conclusion may be drawn, that the precipitate produced by the action of water on this salt is essentially tellurous acid, a small amount of oxychloride of tellurium being present. Hot water dissolves some of this tellurous acid, and, on cooling slowly, the anhydride separates in the characteristic form of colorless octahedra.

Rubidium Tellurichloride, $2RbCl.TeCl_4$. — The preparation of this salt was in every way analogous to that of the cæsium tellurium chloride. However, since this salt is far more soluble than the corresponding cæsium compound, no precipitate was obtained in dilute solutions. The mixture of the hydrochloric acid solution of the constituents was concentrated by evaporation, and, when cooled, crystals separated. These were in the form of octahedra, somewhat larger than the cæsium salt.

	Analysis gave		Calculated for $2RbCl.TeCl_4$.
Rb	33.50	33.83	33.59
Te	24.34	. . .	24.56
Cl	. . .	. . .	41.85

This salt remains permanent in the air. From the dilute hydrochloric acid solution, concentrated hydrochloric precipitates it unaltered. Water decomposes it, evidently in the same way as the cæsium salt.

Potassium Tellurichloride, $2KCl.TeCl_4$. — To prepare this salt in a pure state an excess of tellurium chloride is necessary.

The analyzed material was obtained by spontaneous evaporation of the constituents in a solution of dilute hydrochloric acid, twice as much tellurium chloride being present as required by the formula. Under these conditions it was found to separate in the form of light yellow octahedra, which, under the microscope, were shown to be free from potassium chloride.

	Analysis gave	Ratio.	Calculated for $2KCl.TeCl_4$.
K	17.37	0.44	18.79
Te	30.29	0.24	30.03
Cl	49.47	1.39	51.18
	97.13		

The salt, therefore, has the formula $2KCl.TeCl_4$. The crystals deliquesce somewhat in moist air, and the analyzed material retained a small amount of water, as is shown by the deficiency in the above analysis. It is not probable that the salt contains water of crystallization, for the crystalline form and optical properties show that it is isomorphous with the anhydrous salts. This salt is the most unstable as well as the most soluble of the anhydrous double halides described in this article. It is readily dissolved by dilute hydrochloric acid. Strong hydrochloric acid separates potassium chloride. It therefore cannot be precipitated from its solutions by the addition of strong hydrochloric acid, as in the case of the other chlorides. Alcohol also separates potassium chloride. Water apparently effects the same decomposition as in the case of the cæsium and rubidium chlorides. The tendency of potassium chloride to separate along with the salt explains why Rammelsberg's analysis came high in regard to the potassium chloride. His results corresponded to a mixture of two molecules of KCl and three molecules of $2KCl.TeCl_4$. Experiments with the

calculated quantity of the constituents invariably resulted in the separation of potassium chloride or potassium chloride mixed with the yellow $2KCl.TeCl_4$. Experiments with the method given by Ramsay * for the preparation of this salt, by mixing aqueous solutions of the constituents, resulted in the decomposition of the tellurium chloride, and the resulting white precipitate failed to dissolve until considerable hydrochloric acid was added. Attempts to prepare the compound by concentrating the mixture of the constituents by the aid of heat invariably resulted in failure. In certain cases, on cooling such solutions, a mass of colorless slender prisms was obtained, which have not yet been investigated.

The Double Bromides.

The crystals of the anhydrous bromides have a brilliant red color resembling that of the mineral crocoite. The powders of the salts have a color that is similar to that of a mixture of equal parts potassium bichromate and red lead. The powder of the hydrous bromide has the color of mercuric oxide, but, by loss of water this soon changes to that of the anhydrous salt.

Cæsium Telluribromide, $2CsBr.TeBr_4$. — This double halide can easily be prepared by mixing finely divided tellurium with cæsium bromide in dilute hydrobromic acid, then adding bromine in excess. The presence of free acid is necessary to prevent the separation of tellurous acid. When the tellurium has disappeared, the solution is concentrated by the aid of heat, and, on cooling, bright red crystals of the pure salt are deposited. These are generally somewhat larger than the crystals of the double chloride.

	Analysis gave			Calculated.
Cs . . .	30.90	30.87	30.91	30.54
Te . . .	14.29	13.60	14.03	14.35
Br . . .	55.01	. . .	55.32	55.11

This salt remains unaltered in the air. It can be separated from its solution in dilute hydrobromic acid by the addition

* Loc. cit.

of concentrated acid. It does not melt below the boiling-point of sulphuric acid. Attempts to prepare a hydrous salt according to the methods used for the preparation of $TeBr_4.2KBr.2H_2O$ were without success.

Rubidium Telluribromide, $2RbBr.TeBr_4$. — The directions given for the preparation of the corresponding cæsium compound apply also in the preparation of this salt. If the solutions are strong, the compound separates as a bright red precipitate, but if dilute, on concentrating by means of heat or spontaneous evaporation, it crystallizes in brilliant red octahedra.

	Analysis gave	Calculated.
Rb	22.02	22.04
Te	. . .	16.11
Br	62.07	61.85

This salt is stable in the air. Like the corresponding cæsium salt, this separates from its solutions by the addition of concentrated hydrobromic acid. When it is dissolved in a little water and the solution is cooled slowly, colorless octahedrons of TeO_2 separate. The latter product was found to be impure, containing a small amount of bromine. On heating, the salt decrepitates slightly and melts at a high temperature. Efforts to prepare a hydrous salt according to the methods used for the preparation of $2KBr.TeBr_4.2H_2O$ were without success.

*Potassium Telluribromides, $2KBr.TeBr_4$ and $2KBr.TeBr_4.2H_2O$.** — For the preparation of these salts, a mixture of the constituents was made as described in the case of the cæsium double bromide. The solution invariably deposited crystals of the anhydrous salt when it had been concentrated by heat, but, by spontaneous evaporation of the filtrate, the hydrous salt was obtained. On recrystallizing either of these salts from water or from dilute hydrobromic acid, the anhydrous salt is obtained when the solution has been saturated by boiling and then allowed to cool, but if the solution is left to deposit crystals at ordinary temperature the hydrous modifica-

* Described by Von Hauer as containing three molecules of water of crystallization.

tion is obtained. The crystals of these different compounds closely resemble each other in color and appearance. The anhydrous variety crystallizes in octahedra modified by the cube. The orthorhombic crystals of the hydrous salt look like distorted crystals of the other. This being the case, and since the crystals of the hydrous compound can be obtained much larger than those of the anhydrous salt, both Von Hauer and Wills selected these for their work, while the more easily obtained anhydrous salt was overlooked. The hydrous salt is readily distinguished from the anhydrous one by its deportment on exposure to a dry atmosphere. The latter is stable, but under these conditions the hydrous compound rapidly effloresces, losing its lustre, the faces of the crystals becoming superficially covered with a light reddish yellow and opaque layer of the anhydrous salt. Crystals which have been exposed to dry air for several days and were completely covered with this layer were found, on crushing, to remain unaltered in the interior and to have still retained included water in addition to their water of crystallization. This was shown by the fact that the crushed crystals gave a stain of the mother-liquor to filter paper. This property of the hydrous crystals explains why Von Hauer assigned three molecules of water to this salt instead of two. The material for analysis of the hydrous salt was selected from crystals varying in size from 7 to 13 mm. in diameter. These were very rapidly crushed on smooth filter paper, to remove included water, and immediately corked up in the weighing tube and analyzed. A close examination of the fragments, before and after weighing, gave no evidence of loss of water from the substance by efflorescence. The analyses were from three different crops.

	Analysis gave			Calculated for $2KBrTeBr_4.2H_2O$.	Calculated for $2KBr.TeBr_4.3H_2O$.
K . . .	10.90	11.07	10.73	10.87	10.61
Te . . .	17.59	17.29	17.46	17.38	16.96
Br . . .	66.35	66.36	66.34	66.74	65.11
H_2O . .	5.33	5.53	5.73	5.01	7.32

These results make it evident that the salt contains two molecules of water, and not three as has generally been supposed.

The water in this salt was determined by heating it in an air bath to constant weight. The temperature was maintained between 150°–160°, and finally, to be sure that all the water had been driven off, the residues were analyzed in two cases.

	Analysis gave		Calculated for $2KBr.TeBr_4$.
K	11.71	11.52	11.44
Te	18.29	18.58	18.30
Br	70.25	70.09	70.26

Analyses of products obtained by cooling hot saturated solutions gave the following results:

	Found.			Calculated for $2KBrTeBr_4$.
K	11.67	11.70	. . .	11.44
Te	18.06	. . .	. . .	18.30
Br	70.24	70.20	69.40	70.26

The Double Iodides.

These salts are all black. The powder of the cæsium salt is pure black, that of the rubidium and potassium salts is grayish black.

Cæsium Telluriiodide, $2CsI.TeI_4$. — In order to prepare this salt, and also in the case of the rubidium and potassium compounds, tellurium tetraiodide was made by treating tellurous oxide with hydriodic acid. The iodide of tellurium is sparingly soluble in hydriodic acid, but, on mixing this solution with a solution of cæsium iodide, an amorphous black precipitate was obtained, even in very dilute solutions.

	Analysis gave	Calculated for $2CsI.TeI_4$.
Cs	23.37	23.07
Te	10.51	10.84
I	65.17	66.09

This compound resisted all attempts to prepare it in a crystalline form. It is insoluble in cæsium iodide and in hydriodic acid; hence warming in the mother-liquor failed to dissolve the salt. It is decomposed slowly by cold water, rapidly by hot, and apparently tellurous acid or anhydride separates. This generally is impure, being mixed with a dark-colored residue

containing iodine. On exposure the salt slowly loses iodine. In the open capillary it does not melt below the boiling-point of sulphuric acid.

Rubidium Telluriiodide, $2KbI.TeI_4$. — This compound was prepared by mixing the constituents in the same manner as in the preparation of the corresponding cæsium salt. If the solutions are only moderately concentrated, a black amorphous precipitate is produced. Unlike the corresponding cæsium salt, it dissolves, to a slight extent, on warming in the mother-liquor, and on cooling, black microscopic octahedra are produced.

	Analysis gave	Calculated for $2RbI.TeI_4$.
Rb	16.83	16.17
Te	. . .	11.81
I	72.07	72.02

This iodide is stable on exposure. Water effects the same decomposition as in the case of the cæsium salt. A small portion of this salt dissolves in strong alcohol, giving the color of a weak iodine solution.

Potassium Telluriiodide, $2KI.TeI_4.2H_2O$. — This compound can be prepared most conveniently by boiling tellurium iodide in a strong solution of potassium iodide in dilute hydriodic acid. The solution, filtered while hot from any undissolved tellurium iodide, deposits long black prisms on cooling. These crystals attain considerable size, about 30 mm. in length, when a large excess of potassium iodide is used. The mother-liquor, on evaporation in a desiccator, deposits more of the salt, but the crystals have a different habit.

	Analysis gave			Calculated for $2KI.TeI_4.2H_2O$.
K	8.41	8.50	8.39	7.81
Te	12.25	12.95	12.30	12.48
I	75.97	. . .	76.68	76.11
H_2O . . .	3.57	. . .	. . .	3.60

For the determination of water in this compound the crystals were rapidly pressed on paper and immediately analyzed. It was found that the salt could be dehydrated at a temperature

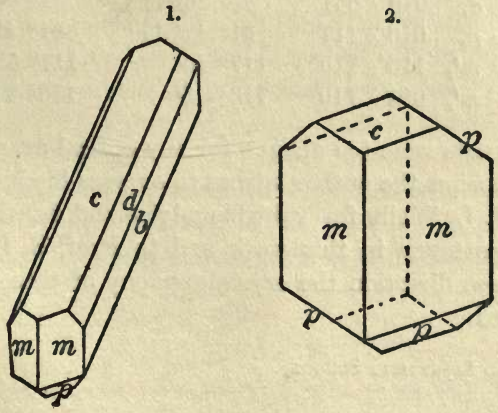
between 110°–115°, the resulting anhydrous salt being stable at that temperature. This was shown by an iodine determination in the residue. Analysis gave 78.78 per cent of iodine; calculated for $2KI.TeI_4$, 78.94.

This salt is far more stable in the air than the corresponding bromide, but the crystals lose their lustre in dry air, becoming dull black on account of a superficial efflorescence.

Crystallography.

The crystallization of the anhydrous alkali-tellurium halides is isometric. The chlorides were obtained in octahedra with little or no modification, the bromides in combination of octahedron and cube. The chlorides and bromides were measured, and also proved to be isotropic by examination in polarized light. Of the anhydrous iodides, the rubidium salt was the only one obtained in crystals, and these were too small to measure, but appeared under the microscope as combination of octahedron and cube. They were so opaque that they could not be tested in polarized light.

The two hydrous salts $2KBr.TeBr_4.2H_2O$ and $2KI.TeI_4.2H_2O$, although analogous to each other in their composition, differ in crystallization. The bromide is orthorhombic, as has been shown by Baker,* also by Grailich and Lang in Rammelsburg's Handbuch.* That the hydrous potassium tellurium



* Loc. cit.

bromide obtained in the present work is identical with that described by the above authors is shown by measurements of the crystals. The crystallization of the salt $2KI.TeI_4.2H_2O$ is monoclinic. Two different habits were observed; long prisms, developed in the direction of the clino axis were obtained from hot solutions (Fig. 1). The mother-liquor from these, on standing, gave shorter prisms in which the domes and clinopinacoids were wanting (Fig. 2).

The forms observed were:

m, 110	*c*, 001	*d*, 031
p, 111	*b*, 010	

The axial ratio is as follows:

$$\dot{a} : \bar{b} : \dot{c} \quad 0.7047 ; \ 1 ; \ 0.5688 \quad B = 100 \wedge 001 = 59° \ 7' \ 16''$$

The crystals gave fair reflections of the signal on the goniometer. Measurements chosen as fundamental are indicated by an asterisk.

		Calculated.	Measured.
$m \wedge m'''$,	$110 \wedge 1\bar{1}0$	62° 20′	62° 26′
$m \wedge b$,	$110 \wedge 010$	58° 50′	*58° 50′
$b \wedge c$,	$010 \wedge 001$	90°	90°
$m \wedge c$,	$110 \wedge 001$	63° 57′	*63° 57′
$m \wedge p$,	$110 \wedge 11\bar{1}$	60° 42′	*60° 42′
$c \wedge p$,	$001 \wedge \bar{1}11$	55° 21′	55° 22′
$b \wedge d$,	$010 \wedge 031$	34° 20′	34° 25′
$b \wedge p$,	$010 \wedge 11\bar{1}$	61° 42′ 49″	61° 42′ 30″
$m \wedge m'$,	$110 \wedge \bar{1}10$	117° 40′	117° 33′
$c \wedge m'$,	$001 \wedge \bar{1}10$	116° 3′	116° 11′

The crystals were too opaque for any optical examination.

In conclusion the author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice and for the interest that he has taken in this work, and to Prof. S. L. Penfield under whose direction the crystallography of these salts was investigated.

SHEFFIELD SCIENTIFIC SCHOOL,
January, 1893.

ON THE AMMONIUM-LEAD HALIDES.*

By H. L. WELLS and W. R. JOHNSTON.

It is a well-known fact that the ammonium double halides, like other ammonium salts, are usually analogous to those of the alkali metals, especially to those of potassium. For example, in connection with an investigation of the cæsium-mercuric halides, made by one of us, † it was noticeable that cæsium compounds were prepared, corresponding to all of the four types of ammonium-mercuric halides that had been previously described.

A study of the cæsium-lead and potassium-lead halides has recently been made in this laboratory, ‡ and, in view of the fact that the existence of four very simple types of double salts was established by that investigation, it seemed desirable to re-investigate the ammonium-lead halides, since a considerable number of these with very complicated formulæ had been described. These peculiar ammonium-lead halides have formed the most noticeable exception to the similarity of the alkali-metal and ammonium salts, and it seems probable that it was chiefly on account of these that Remsen has remarked: § "The position of the double halides containing ammonium is certainly exceptional. They seem to be governed by some law of their own."

All of the extremely complicated ammonium-lead salts have been described by André. ‖

The list of his alleged compounds is as follows:

* Amer. Jour. Sci., xlvi, July, 1893.

† Ibid., xliv, 221. ‡ Ibid., xlv, 121.

§ Amer. Chem. Jour., xi, 296.

‖ Compt. Rend., xcvi, 435 and 1502; Bull. Soc. Chim., (2), xl, 14.

$PbCl_2.18NH_4Cl.4H_2O$	$2PbBr_2.14NH_4Br.3H_2O$
$PbCl_2.10NH_4Cl.H_2O$	$PbBr_2.6NH_4Br.H_2O$
$2PbCl_2.18NH_4Cl.3H_2O$	$7PbBr_2.12NH_4Br.7H_2O$
$PbCl_2.6NH_4Cl.H_2O$	$3PbBr_2.2NH_4Br.H_2O$
$4PbCl_2.22NH_4Cl.7H_2O$	. . . . .
$4PbCl_2.18NH_4Cl.5H_2O$	. . . . .
$4PbCl_2.2NH_4Cl.6H_2O$	. . . . .

From André's original articles, it appeared that he made no mention of having ever prepared any of his remarkable products more than once, and it seems probable that whenever he obtained a crop of crystals or a precipitate he described it as a new compound, without regarding the number of different substances that it might contain. André operated in two ways. A part of his salts were made by dissolving a lead halide in a hot solution of the corresponding ammonium halide and cooling, while the rest were made by dissolving lead monoxide in boiling solutions of ammonium chloride or bromide. From the products made by the last method he obtained lead oxychlorides or oxybromides by heating them with water in sealed tubes. This peculiarity of these products caused him to remark that all the chlorides made in this way seemed to contain some oxychloride. This is the only evidence of any suspicion on his part that he was obtaining mixtures. In a number of instances André describes his products as "crystalline precipitates," "brilliant plates with pearly lustre," "crystallized bodies," etc., so that it would seem that they should have been pure, but after having repeated his experiments, following his methods as closely as his descriptions permitted, with many variations and repetitions, *we are convinced that not one of the salts described by André exists.*

Our work has resulted in the preparation of the following series of salts:

Type 2 : 1.	Type 1 : 1.	Type 1 : 2.
. . . . .	$3NH_4PbCl_3.H_2O$	$NH_4Pb_2Cl_5$
$(NH_4)_2PbBr_4.H_2O$	. . . . .	$NH_4Pb_2Br_5$
. . . . .	$NH_4PbI_3.2H_2O$	. . . . .

For comparison, the potassium series, already referred to, is given:

Type 2 : 1.	Type 1 : 1.	Type 1 : 2.
. . . . .	$3KPbCl_3.H_2O$	KPb_2Cl_5
$K_2PbBr_4.H_2O$	$3KPbBr_3.H_2O$	KPb_2Br_5
. . . . .	$KPbBr_3.H_2O$	. . . .
. . . . .	$KPbI_3.2H_2O$	. . . .

It is to be noticed that the two series correspond exactly, except that no ammonium-lead bromide of the 1: 1 type was obtained. These results show that the ammonium-lead halides are entirely analogous to the potassium salts, and that there is no indication that they are governed by a law of their own.

Returning to the mixtures described as compounds by André, it should be noticed that he came near finding the correct formulæ for three salts. His formula $4PbCl_2 2NH_4Cl.6H_2O$ would be correct if the water were omitted. He should have found two more molecules of NH_4Br in the formula $7PbBr_2.12NH_4Br.7H_2O$ in order to have the salt $(NH_4)_2PbBr_4 H_2O$, and his formula $3PbBr_2.2NH_4Br.H_2O$, in comparison with the errors involved in his more complicated mixtures, is rather near $NH_4Pb_2Br_5$.

Such work as André's is liable to hinder the development of correct chemical theories. A case has been mentioned above where it is probable that his results have been an important factor in causing the ammonium double halides to be looked upon as a class of bodies distinct from the alkali-metal compounds, and it may be mentioned that Carnegie * has used André's formula $PbBr_2.6NH_4Br$ in support of a theory on double halides, although, as must be added, he considers André's more complicated formulæ as inconsistent with his ideas.

We have investigated the ammonium-lead halides by methods which are entirely like those used for the potassium salts, and, in addition, numerous experiments have been made in order to investigate André's methods of preparation. The

* Amer. Chem. Jour., xv, 11.

analytical methods used have been simple. Ammonium was determined by distillation with potash solution and alkalimetry. Lead was determined by treating the substance in a platinum crucible with sulphuric acid, evaporating, igniting and weighing lead sulphate. To determine a halogen, the substance was treated with hot water and an excess of silver nitrate was added; after sufficient digestion, nitric acid was added, and when the precipitate had settled properly it was collected and weighed on a Gooch filter. Water was determined by the loss at 100°, or sometimes at a somewhat higher temperature.

1 : 1 Ammonium-Lead Chloride, $3NH_4PbCl_3.H_2O$. — This is formed by dissolving lead chloride in hot concentrated solutions of ammonium chloride and cooling. Sample A was made by dissolving 25 g. of $PbCl_2$ in 700 c. c. of an ammonium chloride solution which was more than saturated when cold. The double salt was deposited in the form of colorless, transparent, prismatic crystals while the solution was still somewhat warm. Some of the crystals were removed from the warm solution, quickly pressed between smooth filter-papers and air-dried for analysis. On cooling the solution, ammonium chloride crystallized upon the double salt. Sample B was obtained by dissolving 5 g. of PbO in 200 c. c. of a boiling solution of NH_4Cl which was nearly cold-saturated. The last method was suggested by André's experiments.

	Found.		Calculated for $3NH_4PbCl_3.H_2O$.
	A.	B.	
Ammonium . .	5.22– 5.45	. . . . .	5.33
Lead	61.12–60.60	61.84–61.88	61.31
Chlorine . . .	31.78–31.79	31.64	31.56
Water	1.78	. . . . .	1.78

The water in A was determined by heating at about 120° for one hour. The limits of the conditions under which this salt is formed are narrow, for, on slightly diluting the solutions which have given it, the following compound is produced.

1 : 2 Ammonium-Lead Chloride, $NH_4Pb_2Cl_5$. — This salt

is produced under wide limits of conditions. It forms colorless, short, transparent prisms which are usually doubly terminated and are apparently orthorhombic in form. The crystals retain their lustre on drying and are anhydrous.

Four crops were made under the following conditions:

	NH_4Cl. g.	$PbCl_2$. g.	Volume. c. c.
A	100	30	1000
B	100	20	1000
C	200	15	550
D	200	60	700

These crops gave the following analyses:

	Ammonium.	Lead.	Chlorine.
A	2.36–2.67	67.38–67.36	29.08–29.14
B	.....	66.26–67.56	.....
C	.....	66.94–66.76	29.16–29.24
D	.....	68.00–67.28	.....
Calculated for $NH_4Pb_2Cl_5$	2.95	67.93	29.12

Another double chloride was observed, the composition of which was not determined. It will be referred to beyond, under the discussion of André's products.

2 : 1 Ammonium-Lead Bromide, $(NH_4)_2PbBr_4.H_2O$. — This salt is easily prepared by dissolving lead bromide in concentrated solutions of ammonium bromide. Its formation was also observed when lead oxide was dissolved in ammonium bromide by boiling. It forms beautiful radiating groups of highly refracting, slender prisms. Three crops were made as follows:

	NH_4Br. g.	$PbBr_2$. g.	Volume. c. c.
A	200	50	380
B	?	25	260
C	200	50	380

The analyses were as follows:

	Ammonium.	Lead.	Bromine.	Water.
A	6.01–5.86	37.12–36.84	55.06–55.10	2.60
B	. . .	37.06–36.94	54.94	. . .
C	. . .	37.26	. . .	. . .
Calculated for $(NH_4)_2PbBr_4.H_2O$	6.17	35.63	55.08	3.10

1: 2 Ammonium-Lead Bromide, $NH_4Pb_2Br_5$.— On slightly diluting solutions from which the preceding salt would be deposited, this salt is obtained. Repeated trials were made to obtain a 1: 1 salt intermediate between the two, but these were without success. The salt forms square plates, often several millimeters in diameter. The crystals darken somewhat on exposure to light, but they do not lose their lustre on drying, and are evidently originally anhydrous. The compound is formed under rather wide limits of conditions. A single sample was analyzed.

	Found.	Calculated for $NH_4Pb_2Br_5$.
Ammonium . . .	2.17– 2.17	2.16
Lead	49.26–49.12	49.76
Bromine	48.28–48.22	48.08

1: 1 Ammonium-Lead Iodide, $NH_4PbI_3.2H_2O$.— This was the only double iodide obtained, although a thorough search was made for other salts. It forms hair-like crystals of a pale yellow color. Sample A was made by dissolving 100 g. of NH_4I and 10 g. of PbI_2 in sufficient hot water to make a volume of 108 c. c., and cooling. Sample B was obtained by slightly diluting the solution which gave A. It was noticed that where lead iodide was deposited from a moderately concentrated hot solution of ammonium iodide, the lead iodide disappeared on cooling and in its place was formed a compact, silky mass of crystals. Sample C was such a crop as just described, which was carefully separated from the usual form of the double salt which formed above in the solution.

	Found.			Calculated for $NH_4PbI_3.2H_2O$.
	A.	B.	C.	
Ammonium . .	2.40– 2.25	2.97– 2.97	. . .	2.80
Lead	31.08–31.46	31.36–31.20	31.76	32.24
Iodine . . .	59.76–59.70	59.85–59.75	62.45	59.36
Water . . .	5.60	5.65	. . .	5.60

On André's Products.

André prepared some of his most complicated products, such as $2PbCl_4.18NH_4Cl.3H_2O$ and $4PbCl.22NH_4Cl.7H_2O$, by dissolving lead chloride in ammonium chloride solutions and by the use of the corresponding bromides. On repeating his experiments with the bromides, we have not observed anything which did not correspond to the salts which we have described, or to mixtures of these with ammonium bromide. He describes his product $4PbCl_2.22NH_4Cl.7H_2O$ as an abundant precipitate of very brilliant plates with a pearly lustre. We have often observed this beautiful precipitate, but, after many attempts, we have been unable to determine its composition with certainty. It apparently forms only in warm solutions which are almost saturated with ammonium chloride. The prismatic salt $NH_4Pb_2Cl_5$ is usually deposited just before the plates begin to form, and it often forms with them. Large amounts of ammonium chloride often crystallized out when attempts were made to separate the precipitate from the mother-liquor. This happened often even when the solution with the suspended precipitate was poured upon a large mass of filter-paper, so as to soak up the liquid as quickly as possible. Such a crop, which was granular and showed little evidence of being composed of plates, gave 30.50 per cent of lead. By collecting the precipitates, in the manner just described, at an earlier period in the process of their formation, we succeeded in obtaining crops that were apparently pure, but the plates were so exceedingly thin and small, and the mother-liquor was so concentrated, that we had little confidence in the purity of these products. Two such crops gave 51.13 and 53.69 per cent of lead. The formula $(NH_4)_2PbCl_4$ requires 53.77, and it is possible that this may be the true formula for the sub-

stance. It is certain that these two products were practically free from the prismatic salt $NH_4Pb_2Cl_5$, so that it can be positively stated that the ratio of ammonium to lead cannot be greater than 2 : 1 in this compound. André's formula is, therefore, very far from correct. He must have analyzed a mixture of the plates with ammonium chloride. We have found all such mixtures to be anhydrous after being dried in the air for a short time, hence the water in André's formula is remarkable.

A number of attempts were made to obtain the compound in a purer state by warming the solutions and by diluting them slightly, after the precipitates had formed, but these operations left the products open to suspicion, since it was found that further dilution completely decomposed the plates. Several crops, made in this way, gave 59.01, 57.64, 53.69, and 57.80 per cent of lead, which is an insufficient amount for the 1 : 1 anhydrous salt, requiring 62.4. This may be its composition, but it is possible also that it is a dimorphous form of $NH_4Pb_2Cl_5$, for the plates, in being square with diagonal markings, resemble the salt KPb_2Br_5 and other bromides of this type. The undetermined double chloride can be readily prepared by dissolving 160 g. of ammonium chloride and 25 g. of lead chloride in sufficient boiling water to make a volume of 400 c. c. and allowing the solution to cool slowly. The compound often forms in such abundance as to completely fill the solution with a loose mass of the very thin plates.

André's other method of preparing his products was by dissolving lead monoxide in ammonium chloride and bromide solutions. He describes only one complicated bromide, $PbBr_2.6NH_4Br.H_2O$, made in this way. We have made a number of experiments with ammonium bromide and lead oxide without obtaining anything but our own salts and mixtures. Since a number of his chlorides were made by dissolving lead oxide in ammonium chloride solutions, we have made a very careful study of the products obtained by this operation. André sometimes indicates the length of time of boiling the ammonium chloride solution with lead oxide, but is uncertain how

rapidly he boiled his solutions. We have therefore made numerous experiments with wide variations in the amount of ammonia boiled off. Among the various products that we obtained, including the salts that we have described, we frequently noticed a substance that appeared to be new. It was deposited after the solutions had become cold or nearly so, forming brilliant crystals, apparently nearly cubic in form, but so much rounded as to have no distinct faces. These crystals were often 1 or 2 mm. in diameter. They formed upon the bottom and sides of the beaker, adhering firmly to the glass, and their quantity was sometimes such that the walls of the vessel were thickly studded with them. This product evidently corresponded with one of André's, for he says of "$PbCl_2$. $18NH_4Cl.4H_2O$" that it is a very hard crystalline deposit adhering to the glass. We encountered considerable difficulties in obtaining the substance in a pure condition, for it was inclined to deposit upon other things that had previously formed, and it adhered to them as well as to the glass. The first crop analyzed (No. 1) was evidently not pure. Two other crops (2 and 3) appeared better, but still not quite pure. At last, by decanting a solution just before these crystals began to form, we obtained a crop (No. 4), that seemed entirely satisfactory. The following analyses of the four crops were made:

	Ammonium.	Lead.	Chlorine.
No. 1 . . .	28.28	13.44	58.05 = 99.77
No. 2		6.51	. . .
No. 3		6.74	. . .
No. 4		1.08	. . .

The crystals of the last product had exactly the same appearance as the others. It is evident that lead is not an essential constituent of the substance, and that the substance is ammonium chloride crystallized in an unusual form. Analysis No. 1 corresponds to $PbCl_2.24NH_4Cl$. This is not far from André's formula, and it shows what he probably analyzed. It is to be noticed that, while our impure ammonium chloride was practically anhydrous, André gives a considerable amount

of water in his formula. It seems probable that he did not properly dry his products before analyzing them, and, moreover, he evidently determined water from the deficiencies in his analyses. There is more or less water in every one of his formulæ.

Since it was evident that André's operation of boiling ammonium chloride solutions with lead oxide could be imitated, with possibilities for greater variations, by adding ammonia to solutions of lead chloride in ammonium chloride, we have carried out a series of experiments on that plan. No indications of the existence of any of André's complicated compounds were obtained in this way, but, besides the form of ammonium chloride that adheres to the glass, a peculiar modification of it in the form of large, transparent pointed crystals with no distinct faces was observed. A sample of these contained 3.23 per cent of lead. When much ammonia was used in these experiments, an oxychloride of lead was obtained. A pure product of this was prepared by saturating a cold-saturated solution of ammonium chloride with lead chloride while boiling, then adding an equal volume of the cold-saturated ammonium chloride solution and finally adding a large excess of ammonia. A precipitate was formed and re-dissolved by the ammonia. The oxychloride was deposited, on cooling, in the form of small, blade-like, transparent crystals. Analysis showed that it was the compound PbClOH.

	Found.	Calculated for PbClOH.
Lead	79.17	79.77
Chlorine	14.06	13.68
Oxygen	[2.72]	3.08
Water	4.05	3.47

This compound has long been well known, having been used as a white pigment. It is worthy of remark that André redescribed this body correctly in one of his papers that has already been referred to.* He made it by heating a small quantity of "$PbCl_2NH_4Cl.H_2O$" with water in a sealed tube.

* Bull. Soc. Chim., II, xl, 15 (1883).

It is evident that such a product could not have been produced if the chlorides had not contained some basic substance.

Experiments with Ammonium Chloride and Lead Iodide.

Poggiale * and Völkel † have each described a mixed double halide of ammonium and lead, neither of which agrees with the types of unmixed halides which we have described in this article. Poggiale's formula is $PbI_2.4NH_4Cl.2H_2O$, while Völkel's is $PbI_2.3NH_4Cl$. It is evident that the two investigators obtained the same compound, for both made their products in essentially the same way, and both describe them as occurring in the form of silky needles. We have repeated the experiment of dissolving lead iodide in ammonium chloride solutions and have readily obtained the silky crystals. The product resembles exactly the salt $NH_4PbI_3.2H_2O$, except that it is considerably paler in color than the latter. An analysis of a pure product, carefully dried by pressing with paper, showed that the formulæ of both Poggiale and Völkel are incorrect, and that their products must have been contaminated with ammonium chloride. The salt corresponds in type to our double iodide. It loses one molecule of water on exposure to the air for two or three days, becoming much darker in color; the second molecule of water goes off at 100°.

	Found.	Calculated for $NH_4Cl.PbI_2.2H_2O$.
Ammonium . . .	3.33	3.27
Lead	34.83–34.68	37.60
Chlorine	5.11– 5.10	6.45
Iodine	51.08–50.94	46.14
Water	5.35	6.54

The analysis indicates that the lead iodide and ammonium chloride do not combine quite unchanged, and that the formula $NH_4Pb(Cl,I)_3.2H_2O$ possibly expresses the composition of the product better than the one given above. In the course of our experiments with ammonium chloride and lead iodide, we obtained a crop of crystals which showed an almost complete

* Compt. Rend., xx, 1180. † Pogg. Ann., lxii, 252.

replacement of the iodine by chlorine. The salt was a 1 : 2 compound, a type which apparently does not exist among the double iodides of lead. It gave the following analysis:

	Found.	Calculated for $NH_4Pb_2Cl_5$.
Ammonium	. . .	2.95
Lead	66.82	67.93
Chlorine	28.76	29.12
Iodine	1.44	. . .

The view that certain mixed lead double halides are to be considered as variable mixtures of two isomorphous, unmixed double halides was arrived at by Wells and Wheeler * from experiments with cæsium chloride and lead bromide. Herty † has more recently arrived at the same conclusion from his investigation of the mixed double bromide and iodide of potassium and lead. It is not safe to conclude, however, because definite mixed double halides do not occur in some cases, that they are never formed. It is certain that there is a tendency toward the formation of such definite compounds in many cases. For example, it is to be noticed that in the above analysis of $NH_4Cl.PbI_2.2H_2O$ there is only a slight variation from the composition required by the formula, while, from a solution of the same ingredients, another type of salt was deposited which was almost free from iodine. The compound $Cs_2HgCl_2I_2$, ‡ described by one of us, is evidently a definite mixed double halide which is not intermediate in its properties between the corresponding chloride and iodide, and which has a constant composition. A number of other cæsium-mercuric halides were described, which approached a constant composition when made under varying conditions.

SHEFFIELD SCIENTIFIC SCHOOL,
March, 1893.

* Amer. Jour. Sci., lxv, 129.
† Amer. Chem. Jour., xv, 81.
‡ Amer. Jour. Sci., xliv, 232.

ON THE RUBIDIUM-LEAD HALIDES, AND A SUMMARY OF THE DOUBLE HALIDES OF LEAD.*

By H. L. WELLS.

THE cæsium-lead and potassium-lead halides have already been studied in this laboratory, and an account of the ammonium compounds is given in the preceding article. It has therefore seemed desirable to make an investigation of the rubidium salts in order to make the work more complete.

2 : 1 Rubidium-Lead Chloride, $2Rb_2PbCl_4.H_2O$. — This was formed by dissolving lead chloride in a solution of rubidium chloride which was so concentrated as to be almost saturated when cold. It forms colorless, transparent, slender, flat prisms which retain their lustre on exposure to the air. Two separate crops were analyzed.

	Found.		Calculated for $2Rb_2PbCl_4.H_2O$.
Rubidium . . .	29.63	29.85	32.39
Lead	41.41	41.75	39.20
Chlorine. . . .	26.73	26.84	26.90
Water	2.29	2.01	1.51
	100.06	100.45	100.00

The amount of water in the salt seems somewhat uncertain, but, since there was no evidence of loss of water by efflorescence and since the salt was simply air-dried without being pulverized, the above formula is preferred to $Rb_2PbCl_4.H_2O$, which requires 2.99 per cent of water. The water was determined by heating to about 200°; at 100° the salt lost only about one quarter of its water in twelve hours.

1 : 2 Rubidium-Lead Chloride, $RbPb_2Cl_5$. — This compound forms small, prismatic crystals which are usually

* Amer. Jour. Sci., xlvi, July, 1893.

grouped side by side in nearly parallel position. It is produced from solutions which are more dilute than those from which the preceding salt is prepared, and it is formed under rather wide limits of conditions. Two separate crops gave the following analyses:

	Found.		Calculated for $RbPb_2Cl_5$.
Rubidium . . .	13.09	12.68	12.63
Lead	60.57	61.05	61.15
Chlorine . . .	26.19	26.29	26.22
	99.85	100.02	100.00

2 : 1 Rubidium-Lead Bromide, $2Rb_2PbBr_4.H_2O$. — This salt resembles the corresponding chloride, both in its formation and appearance. Two crops gave the following analyses:

	Found.		Calculated for $2Rb_2PbBr_4.H_2O$.
Rubidium . . .	23.17	22.73	24.19
Lead	30.29	30.81	29.29
Chlorine . . .	. . .	45.04	45.26
Water	1.55	1.51	1.27
		100.09	100.00

1 : 2 Rubidium-Lead Bromide, $RbPb_2Br_5$. — This forms square plates. It is readily prepared, since it is formed under considerable variations of conditions.

	Found.	Calculated for $RbPb_2Br_5$.
Rubidium . . .	9.81	9.50
Lead	45.74	46.03
Bromine	44.62	44.47
	100.17	100.00

1 : 1 Rubidium-Lead Iodide, $RbPbI_3.2H_2O$. — This is the only double iodide that could be produced under widely varying conditions. It forms very slender, hair-like prisms of a pale yellow color. It rapidly loses its water when exposed to the air, undergoing a remarkable change of color. The pale yellow compound quickly assumes an orange color, then the color becomes almost like that of the original salt. It is evident that the salt, which contains two molecules of water, loses a part of this, probably one molecule, with change of color to orange; then the remainder of the water is lost with

another change of color. It is interesting to notice, in this connection, that the salt $NH_4PbClI_2.2H_2O$ undergoes a similar change of color, as far as the first step is concerned, on losing one molecule of water when it is exposed to the air, but this salt does not lose its second molecule at ordinary temperatures. A sample of the rubidium-lead iodide was rapidly pressed on paper until some of the particles began to show a change of color to orange. Water was determined in this sample from the loss at 100°.

	Found.	Calculated for $RbPbI_3.2H_2O$.
Water	6.09	5.07

An air-dry sample gave the following analysis:

	Found.	Calculated.
Rubidium . . .	13.29	12.70
Lead	28.95	30.73
Iodine	56.80	56.57
	99.04	100.00

Summary.

The following table gives a list of the lead double halides which have been prepared in this laboratory. All of them were new compounds except $KPbBr_3.H_2O$ and $KPbI_3.2H_2O$, these having been previously described by Remsen and Herty.

4 : 1	2 : 1	1 : 1	1 : 2
Cs_4PbCl_6	. . . . .	$CsPbCl_3$	$CsPb_2Cl_5$
Cs_4PbBr_6	. . . . .	$CsPbBr_3$	$CsPb_2Br_5$
. . . . .	. . . . .	$CsPbI_3$	. . . . .
. . . . .	$2Rb_2PbCl_4.H_2O$	. . . . .	$RbPb_2Cl_5$
. . . . .	$2Rb_2PbBr_4.H_2O$	. . . . .	$RbPb_2Br_5$
. . . . .	. . . . .	$RbPbI_3.2H_2O$	. . . . .
. . . . .	. . . . .	$3KPbCl_3.H_2O$	KPb_2Cl_5
. . . . .	$K_2PbBr_4.H_2O$	$3KPbBr_3.H_2O$	KPb_2Br_5
. . . . .	. . . . .	$KPbBr_3.H_2O$	. . . . .
. . . . .	. . . . .	$KPbI_3.2H_2O$	. . . . .
. . . . .	. . . . .	$3NH_4PbCl_3.H_2O$	$NH_4Pb_2Cl_5$
. . . . .	$(NH_4)_2PbBr_4.H_2O$	. . . . .	$NH_4Pb_2Br_5$
. . . . .	. . . . .	$NH_4PbI_3.2H_2O$	. . . . .
. . . . .	. . . . .	$NH_4PbClI_2.2H_2O$	. . . . .

An inspection of the table shows that the cæsium salts differ from the others in including the 4 : 1 type and in being without any 2 : 1 salts. It is quite probable that we have not succeeded in preparing all the salts that are possible, but it seems certain that the 4 : 1 rubidium, potassium, and ammonium salts cannot be made on account of the comparative insolubility of the simple halides. The cæsium salts also differ from the others in being all anhydrous. The hydrous rubidium salts have less water or lose it more readily than the potassium compounds. $KPbI_3.2H_2O$ is stable in the air, but $RbPbI_3.2H_2O$ loses its water readily. There is evidently a gradation, in affinity for water, from the cæsium to the potassium compounds. A gradation in water, from the chloride to the iodide, apparently exists in the potassium and ammonium compounds of the 1 : 1 type. That such gradations in water exist among the double halides, increasing with the atomic weight of the halogens and decreasing with the atomic weight of the alkali metals, has already been observed by Remsen.*

The simplicity of the ratios in the four types of double halides of lead is noticeable. The 4 : 1 type, according to Werner's remarkable theory, † may be considered as the ideal type of a double halide of an alkali metal and a bivalent metal, and as the limit beyond which the ratios of alkali metal to lead cannot go. The type is represented, as Werner mentions, by numerous double cyanides of bivalent metals, such as $K_4Fe(CN)_6$ and by other salts, such as K_4CdCl_6.

The number of 2 : 1 lead salts that we have prepared is rather small, but this is a very common type among the known double halides of the other bivalent metals.

The number of 1 : 1 lead salts is the largest of all. It is remarkable that all the double iodides belong to this type. This is also a well-known type of bivalent metal double halides. It is noticeable that the salt $CsPbBr_3$ is dimorphous, while three mercuric salts of the same type, ‡ $CsHgCl_3$, $CsHgBr_3$, and $CsHgClBr_2$ are also dimorphous.

* Amer. Chem. Jour., xiv, 88. † Zeitschr. anorg. Chem., iii, 281.
‡ Amer. Jour. Sci., xliv, 222.

The 1 : 2 salts are all anhydrous, and a chloride and bromide were prepared with each of the alkali metals and with ammonium. They are formed under wide limits of conditions and are therefore very easily prepared. It is noticeable that the rubidium, potassium, and ammonium chlorides of this type all crystallize in prisms, while all the bromides and the chloride containing cæsium crystallize in plates. A number of other double halides of this type are known, especially among the mercuric compounds. Herty has evidently prepared a potassium-lead double halide of the 1 : 2 type containing bromine and iodine, although he interprets his results in an entirely different way. In a recent article * he describes some tabular crystals of an olive-green color which he has selected and analyzed with evident care and skill. He gives the following analyses of three separate products:

	Pb.	I.	Br.	K.
p. 95, D . .	44.89	17.61	32.59	4.56 = 99.65
p. 95, E . .	45.42	14.94	34.72	4.50 = 99.58
p. 104 . .	43.87	22.20	29.03	4.43 = 99.53

The following ratios may be derived from the above analyses:

	Pb :	I + Br :	K.
p. 95, D . . .	2.	5.01	1.07
p. 95, E . . .	2.	5.15	1.08
p. 104	2.	5.08	1.08

The ratio required for the formula $KPb_2(Br,I)_5$ is Pb: I + Br: K = 2 : 5 : 1, and the agreement is so close that there can be no doubt that this is the formula. Although no pure iodide of this type has been produced, it is interesting to notice that Herty's compound shows that the potassium salt is capable of existence when mixed with a relatively large amount of the bromide.

SHEFFIELD SCIENTIFIC SCHOOL,
March, 1893.

* Amer. Chem. Jour., XV, pp. 94, 95, 97-99, 103, 104 (February, 1893).

ON THE DOUBLE HALIDES OF ARSENIC WITH CÆSIUM AND RUBIDIUM; AND ON SOME COMPOUNDS OF ARSENIOUS OXIDE WITH THE HALIDES OF CÆSIUM, RUBIDIUM, AND POTASSIUM.*

By H. L. WHEELER.

No compounds of arsenious halides with alkaline halides have been definitely described. Nicklès†, in his work on the bromides and iodides of arsenic, antimony, and bismuth, states that these salts combine with alkaline bromides and iodides respectively, but in the case of arsenic he gives no analyses of the compounds which he obtained, and he does not describe the methods that he used in preparing them. He does not even state with what alkaline halides he performed his experiments. Emmet,‡ Harms,§ Schiff, and Sestini‖ have described compounds of arsenious oxide with potassium halides, but this class of bodies has been most thoroughly studied by Rüdorff.¶ His results indicate the existence of two types of this class of compounds, the first containing one molecule of alkaline halide to one of arsenious oxide, the other having these constituents in the ratio 1 : 2. In the present investigation a complete series of the cæsium and rubidium oxyhalides of the 1 : 1 type was obtained, while the formation of the 1 : 2 type was not observed. There is evidently a gradation in stability from the oxychlorides to the oxyiodides, the stability increasing with increasing atomic weight of the halogens. Attempts to prepare double halides of pentavalent arsenic were without success.

* Amer. Jour. Sci., xlvi, August, 1893.

† Compt. Rend., xlviii, 839; Jour. Pharm., III, xli, 142; Rép. chim. pure, i, 366.

‡ Amer. Jour. Sci., I, xviii, 58. § Ann. Chem. Pharm., xci, 371.

‖ Ibid., 228, 72.

¶ Ber. d. Deutsch. Chem. Ges., xix. 2668; Ibid., xxi, 3053.

The new compounds to be described in this article are the following:

$3CsCl.2AsCl_3$	$3CsBr.2AsBr_3$	$3CsI.2AsI_3$
$3RbCl.2AsCl_3$	$3RbBr.2AsBr_3$	$3RbI.2AsI_3$
$CsCl.As_2O_3$	$CsBr.As_2O_3$	$CsI.As_2O_3$
$RbCl.As_2O_3$	$RbBr.As_2O_3$	$RbI.As_2O_3$

The compound $As_2O_3.KI$, which had not been observed by Rüdorff,* was obtained in attempts to prepare a double iodide of potassium and arsenic.

It is to be noticed that only one type of double halides was obtained. This type corresponds to the most readily prepared double chloride of cæsium with antimony, described by Remsen and Saunders † and of cæsium and bismuth, described by Remsen and Brigham.‡ Many attempts were made to prepare arsenic double halides of other types than this single one, but these have invariably been without success, although several types of antimony and bismuth double halides have been described.

It has been shown in several instances by Wells and Wheeler § that cæsium and rubidium halides form more stable or more complete series of double salts than the halides of the other alkali metals. This fact is again well illustrated in the double halides of arsenic, for the cæsium and rubidium double halides are prepared without difficulty, while with potassium no double halides were obtained.

Methods of Preparation.

To prepare the double halides, a strong acid solution is necessary, in order to prevent the decomposition of the arsenious halide and the consequent formation of oxy-compounds. The double halides are less soluble in the strong than in the dilute halogen acids. Excess of one or the other of the constituents has no effect on the composition of the products

* Loc. cit.

† Amer. Chem. Jour., xiv, 152.

‡ Ibid., p. 164.

§ Amer. Jour. Sci., III, xliii, 475; III, xliv, 42.

obtained. The formation of As_2O_3 compounds was observed on treating the double halides or a solution of the constituents in strong acids, with water or dilute acids. The oxygen compounds are difficultly soluble in dilute acids; strong acids convert the cæsium and rubidium compounds into the double halides.

Method of Analysis.

The salts were filtered on the pump, and without delay were carefully freed from the mother-liquor by pressing on paper. They were then dried in the air. In no case was water used to wash them. In order to determine arsenic the salt was dissolved in the cold in HCl sp. gr. 1.1, and hydrogen sulphide passed in for about one hour; then a little alcohol was added, the whole was warmed on the water bath for a short time, in order to drive off the excess of hydrogen sulphide and effect the separation of the last traces of arsenious sulphide. The sulphide of arsenic was collected on a Gooch filter, and after washing with water, alcohol, and carbon disulphide it was dried at 100° and weighed. Sulphuric acid was added to the filtrate, and the alkali metal determined as normal sulphate by evaporating and igniting the residue in a stream of air containing ammonia. The halogens were determined in a separate portion as silver halides in the usual manner.

Cæsium and Rubidium Arsenious Chlorides, $3CsCl.2AsCl_3$ and $3RbCl.2AsCl_3$. — These have a pale yellow color, like the corresponding antimony and bismuth double chlorides. The cæsium salt was obtained by dissolving 250 g. of CsCl in dilute HCl. 2 g. of As_2O_3 in dilute HCl were then added. This produced a precipitate which dissolved on the addition of about 2 liters of hot HCl sp. gr., 1.1. On cooling, light yellow crystals were deposited. A portion of these was recrystallized from a strong HCl solution of $AsCl_3$. The rubidium salt was prepared in the same manner, except that much stronger solutions were required. Saturated solutions of rubidium and arsenic chlorides in 20 per cent HCl produce no precipitate on mixing, but if concentrated HCl is added.

brilliant spangles of the double salt separate. The analysis of these products gave:

	Prepared with Excess of CsCl.		Prepared with Excess of $AsCl_3$.	Calculated for $3CsCl.2AsCl_3$.
Cs	46.14	45.27	45.09	45.94
As	17.15	...	17.11	17.27
Cl	36.89	36.74	36.12	36.79

	Found.	Calculated for $3RbCl.2AsCl_3$.
Rb	35.55	35.33
As	20.14	20.66
Cl	44.04	44.01

Both salts can be recrystallized from hydrochloric acid of sp. gr. 1.1. 100 parts of HCl sp. gr. 1.2 dissolve .429 parts of the cæsium salt and 2.935 parts of the rubidium compound. Since the corresponding potassium salt apparently does not exist, these solubilities suggest a convenient method for obtaining cæsium and rubidium free from potassium.

Cæsium and Rubidium Arsenious Bromides, $3CsBr.2AsBr_3$ and $3RbBr.2AsBr_3$. — These are amber-yellow, the shade being somewhat darker than that of the chlorides. They are most conveniently prepared by using an excess of the alkaline halide. Strong hot solutions of the alkaline bromides were made in about 40 per cent HBr. On adding crystals of $AsBr_3$ these melted, but soon solidified to a yellow mass of the double halide. This dissolved on boiling, and, on cooling, brilliant yellow crystals were obtained. These compounds can be recrystallized unaltered from strong HBr. Analysis gave:

	Found.	Calculated for $3CsBr.2AsBr_3$.
Cs	31.91	31.44
As	11.89	11.82
Br	56.94	56.74

	Prepared with Excess of RbBr.	Prepared with Excess of $AsBr_3$.	Calculated for $3RbBr.2AsBr_3$.
Rb	23.35	...	22.77
As	12.55	...	13.31
Br	63.97	64.43	63.92

Cæsium and Rubidium Arsenious Iodides, $3CsI.2AsI_3$ and $3RbI.2AsI_3$. — These are deep red, the larger crystals of the cæsium compound are more opaque and appear black. To prepare these compounds the normal alkaline iodides were dissolved in strong colorless hydriodic acid, and these solutions were then saturated boiling with crystals of AsI_3. Unless the hydriodic acid is decolorized the product obtained in the case of the cæsium salt is generally impure, being mixed with CsI_3.*

A well-crystallized product of the double cæsium salt was obtained by preparing the salt in the presence of considerable alcohol. Analysis of these compounds gave

	Found.	Calculated for $3CsI.2AsI_3$.		Found.		Calculated for $3RbI.2AsI_3$.
Cs . .	24.38	23.58	Rb . .	16.86	. . .	16.55
As . .	8.92	8.87	As . .	9.96	10.60	9.68
I . . .	67.23	67.55	I . . .	73.65	. . .	73.77

An attempt was made to prepare potassium arsenious chloride by mixing solutions of potassium chloride and arsenious acid, saturated solutions of these substances in concentrated HCl being used for the purpose. No precipitate was thus produced, and, on concentrating the solution, potassium chloride was deposited. Aqueous solutions of potassium chloride, when added to solutions of arsenic trioxide in concentrated HCl, gave precipitates consisting chiefly of As_2O_3. Analogous experiments with potassium bromide and arsenious bromide gave similar results, and operating in the same way with KI and AsI_3 in concentrated HI solutions, nothing but crystals of AsI_3 or mixed crops of AsI_3 and KI were obtained. Similar negative results, in respect to the formation of double halides of ammonium and arsenic, have been obtained by Wallace.†

Compounds of Arsenic Trioxide with Alkaline Halides, $Cs\,Cl.As_2O_3$ and $Rb\,Cl.As_2O_3$. — When a hot saturated aqueous solution of 25 g. of cæsium chloride was saturated with $3CsCl.2AsCl_3$, a finely divided white precipitate was formed on

* Am. Jour. Sci., xliii, 17; Zeitschr. anorg. Chem., i, 85.

† Phil. Mag., IV, xvi, 358; xvii, 122, 261.

cooling (analysis 1). When 6.5 g. of the double chloride were dissolved in 800 c. c. of a cold-saturated solution of As_2O_3 in HCl sp. gr. 1.1 by the aid of heat, a similar precipitate was obtained (analysis 2). Products intermediate in composition were obtained by recrystallizing the double halide from water (analysis 3), from 10 per cent HCl (analysis 4), and from 15 per cent HCl (analysis 5).

	1.				2.	3.
Cs . . .	41.51	41.85	41.75	41.80	25.56	34.29
As . . .	35.59	34.58	35.37	. . .	47.64	43.05
Cl	11.46	. . .	11.31	. . .	11.64	8.86
O	[11.44]	. . .	[11.57]	. . .	[15.16]	[13.80]

	4.	5.	Calculated for $CsCl.As_2O_3$.
Cs	35.30	33.92	36.29
As	39.14	38.10	40.93
Cl	10.63	11.42	9.68
O	[14.93]	[16.56]	[13.10]

The analyses show a considerable variation from the composition required by the formula, the products made under the extreme conditions giving ratios of arsenious oxide to cæsium chloride of 3 : 4 and 3 : 2 instead of 1 : 1. The conditions varied so widely, however, that it seems fair to assume the existence of a 1 : 1 compound.

When the double chloride of rubidium was recrystallized from about 15 per cent HCl, a white crystalline crust was obtained on slowly cooling. This gave analytical results agreeing with the formula $RbCl.As_2O_3$.

	Found.	Calculated for $RbCl.As_2O_3$.
Rb	26.90	26.80
As	. . .	47.03
Cl	11.41	11.13
O	. . .	15.04

Under the microscope these compounds appear as irregular grains or plates, of indefinite crystalline form.

$CsBr.As_2O_3$ and $RbBr.As_2O_3$. — When the double bromides are recrystallized from water, or dilute HBr, they yield these oxy-compounds, and these generally separate in the form of a white crust on the bottom and sides of the beaker. Analysis of such products gave:

	$3CsBr.2AsBr_3$ recrystallized from Water.	$3CsBr.2AsBr_3$ recrystallized from CsBr Solution.	Calculated for $CsBr.As_2O_3$.
Cs	32.42	. . .	32.36
As	36.52	. . .	36.50
Br	19.57	19.59	19.46
O	[11.49]	. . .	11.68

	$3RbBr.2AsBr_3$ from dilute HBr.	$3RbBr.2AsBr_3$ from Water.	Calculated for $RbBr.As_2O_3$.
Rb	24.24	16.56	23.52
As	40.06	50.74	41.27
Br	24.53	15.91	22.01
O	[11.17]	[16.79]	13.20

It is to be noticed that the product obtained by recrystallizing $3RbBr.2AsBr_3$ from water is impure, while the cæsium compound made in the same way corresponds to the formula. This is an illustration of the greater tendency of the cæsium halide to form double salts than in the case of the rubidium halide. Both these compounds are white, but the rubidium compound turns somewhat yellow on drying. Under the microscope, six-sided plates were seen in the case of the cæsium compound when the solution was slowly cooled. There were also observed hexagonal crystals with a short columnar rhombohedral habit. They were uniaxial with weak, negative double refraction. The rubidium compound was also obtained in hexagonal crystals showing rhombohedral symmetry and weak negative double refraction.

$CsI.As_2O_3$, $RbI.As_2O_3$ and $KI.As_2O_3$. — The formation of these compounds was observed when dilute hydriodic acid solutions of the alkaline iodides were mixed with dilute acid solutions of AsI_3. If the solutions are mixed while hot, these double salts separated on cooling in the form of crystal-

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line yellow crusts on the bottom and sides of the beaker. These crystals are generally somewhat larger than those of the compounds of As_2O_3 with the chlorides and bromides. Under the microscope they exhibited the form of six-sided plates. These show a strong negative double refraction.

The potassium compound also appeared in the form of six-sided plates; these remained dark when rotated between crossed nicols. They were too small to afford an axial figure, as the largest plates did not exceed 0.01 mm. in diameter. They are probably hexagonal. Analyis gave:

	Found.	Calculated for $CsI.As_2O_3$.
Cs	29.31	29.04
As	32.01	32.75
I	28.94	27.73
O	[9.74]	10.48
		Calculated for $RbI.As_2O_3$.
Rb	20.35	20.83
As	36.78	36.54
I	31.94	30.93
O	[10.93]	11.70
		Calculated for $KI.As_2O_3$.
K	10.75	10.74
As	42.85	41.20
I	34.13	34.88
O	[12.27]	13.18

Crystallography.

The crystallization of the cæsium and rubidium arsenious halides is hexagonal. They were all measured and found to be isomorphous. In general the habit was holohedral, although in the case of cæsium arsenious bromide it is rhombohedral. All these salts show a pronounced basal cleavage, and plates parallel to this, examined with the stauroscope, are uniaxial: the double chlorides and bromides show a weak negative double refraction, while the double iodides are positive. The forms observed are as follows:

c	0001	O	r	$10\bar{1}1$	1
a	$11\bar{2}0$	i-2	z	$01\bar{1}1$	−1
m	$10\bar{1}0$	I	p	$20\bar{2}1$	2

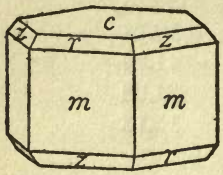
The steep pyramid p was found only on the iodides.

The following table gives the lengths of the vertical axes:

	a	:	c
$3CsCl.2AsCl_3$ . . .	1		1.209
$3RbCl.2AsCl_3$ . . .	1		1.210
$3CsBr.2AsBr_3$ . . .	1		1.219
$3RbBr.2AsBr_3$ . . .	1		1.220
$3CsI.2AsIs_3$ . . .	1		1.244
$3RbI.2AsI_3$	1		1.243

A comparison of the above axial ratios shows the interesting fact that the substitution of rubidium for cæsium produces no appreciable effect in the lengths of the axes, and that in this series the vertical axes lengthen as the atomic weight of the halogens increases. The crystals were sufficiently stable to yield good measurements, although on long exposure they usually lose their lustre. In the lists of measurements the angles chosen as fundamental are noted by an asterisk.

1.



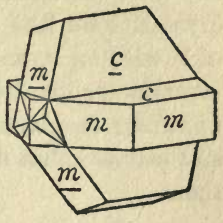
$3CsCl.2AsCl_3$. — This salt was made in crystals about 1–2 mm. in diameter. The forms observed are m, a, r, z, and c. A careful search was made for indications of a rhombohedral development of the faces r and z, but none was found. Apparently they are always holohedral in their development, Fig. 1.

	Measured.	Calculated.
$m \wedge c$, $10\bar{1}0 \wedge 0001$	90°	90°
$c \wedge r$, $0001 \wedge 10\bar{1}1$	*54° 24′	. . .
$r \wedge m$, $11\bar{1}1 \wedge 1010$	35° 39′	35° 36′
$m \wedge z$, $10\bar{1}0 \wedge 01\bar{1}1$	66° 3′	66° 1′
$r \wedge z$, $10\bar{1}1 \wedge 01\bar{1}1$	47° 53′	47° 58′

There is a rather poor prismatic cleavage, and plates parallel to this show parallel extinction.

3RbCl.2AsCl$_3$. — This salt was made in crystals up to about 5 mm. in diameter. The forms observed are *c*, *m*, *r*, and *z*. The faces *r* and *z* were seldom present, but when these did occur it could not be seen whether they exhibited rhombohedral symmetry or not. Penetration twins are common, the twinning plane being the rhombohedron $0\bar{1}11$, Fig. 2.

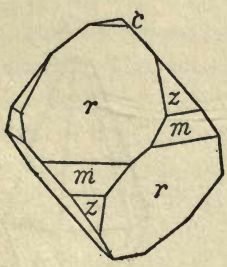
2.



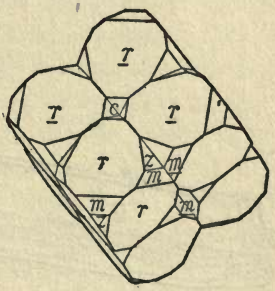
		Measured.	Calculated.
$c \wedge c$ (twin),	$0001 \wedge 0001$	*71° 3′	
$c \wedge r$,	$0001 \wedge 10\bar{1}1$	54° 21′	54° 28½′
$m \wedge r$,	$10\bar{1}0 \wedge 10\bar{1}1$	35° 39′	35° 31½′

On examining this salt in convergent polarized light a uniaxial cross is seen whose arms are not black but a deep and brilliant blue, the character being negative. When examined in monochromatic red light, the crystals are nearly isotropic, the double refraction being extremely weak and probably negative. In blue light, however, a distinct cross is seen accompanied by axial rings. This difference between red and blue explains the colored cross seen in white light. Sections parallel to the axis *c* show the deep peculiar blue characteristic of uniaxial bodies with the above-mentioned optical properties.

3.



4.


r
r
r

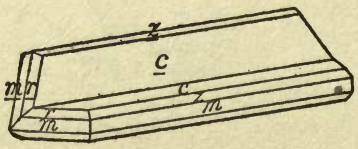
This is the only salt of the series that has a rhombohedral habit, and as the angle of the rhombohedron is nearly 90° the crystals look like cubes. Fig. 3 shows an ideal combination of r with m, z, and c. This form was not observed, as the crystals are invariably twins. An ideal representation of the twinning is given in Fig. 4. The r faces were so curved and striated that no exact measurements could be made from them.

	Measured.	Calculated.
$m \wedge z$, $01\bar{1}0 \wedge 01\bar{1}1$	*35° 23′	. . .
$z \wedge z$, $10\bar{1}1 \wedge \bar{1}101$	. . .	89° 50′

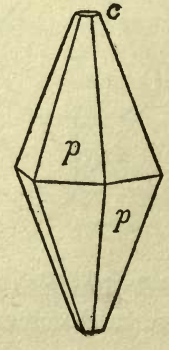
3RbBr.2AsBr$_3$. — This salt was made in small crystals, up to 2 mm. in diameter. The forms observed were c, m, and r. The crystals were made in two habits. When prepared with an excess of RbBr, it separates in prismatic crystals which resemble the form of cæsium arsenious chloride, Fig. 1. In one experiment, by using an excess of $AsBr_3$, contact twins were obtained. Here the twinning plane is the unit rhombohedron, as in Fig. 2, but some of the faces are lengthened parallel to the edge between the two basal planes (Fig. 5).

	Measured.	Calculated.
$c \wedge c$ (twin), $0001 \wedge 0001$	70° 45′	70° 44′
$c \wedge r$, $0001 \wedge 10\bar{1}1$	54° 40′	54° 38′
$r \wedge m$, $1011 \wedge 10\bar{1}0$	*35° 22′	. . .
$r \wedge z$, $1011 \wedge 01\bar{1}1$	48° 14′	48° 7½′
$m \wedge z$, $10\bar{1}0 \wedge 01\bar{1}1$	65° 34′	65° 56′

5.



6.



3CsI.2AsI$_3$. — This salt was made in beautiful crystals up to 3 mm. in length. The forms observed are *p* and *c*. The habit is that of a steep doubly terminated hexagonal pyramid, with the basal planes small or wanting. Often the middle edges are rounded by oscillatory combinations of the pyramids giving rise to horizontal striations. There was no indication of a prism or of a rhombohedral development of the pyramidal faces.

	Measured.	Calculated.
$c \wedge p$, $0001 \wedge 20\bar{2}1$	*70° 49′	. . .
$p \wedge p$, $20\bar{2}1 \wedge 2\bar{0}2\bar{1}$	38° 19′	38° 22′
$p \wedge p$, $20\bar{2}1 \wedge 02\bar{2}1$	56° 24½′	56° 21′ 34″

This salt is without optical anomalies, and no pleochroism was observed.

3RbI.2AsI$_3$. — This salt was prepared in very small crystals, not over 1 mm. in length. The forms observed were *c*, *m*, and *p*. The habit is similar to Fig. 6, but usually the middle edges are replaced by the faces of the prism *m* or are rounded by horizontal striations.

	Measured.	Calculated.
$p \wedge p$, $20\bar{2}1 \wedge 02\bar{2}1$	*56° 21′	. . .
$c \wedge p$, $0001 \wedge 20\bar{2}1$	70° 47′	70°
$p \wedge m$, $20\bar{2}1 \wedge 10\bar{1}0$	19° 12′	20° 56′

Optically this salt shows anomalies. Basal cleavage plates between crossed nicols are not dark, but light and remain so during revolution. In convergent light the locus of an optic axis is seen in the centre of the field coinciding with the vertical axis *c*. The bisectrix lying nearest this axis is that of least elasticity, C. The salt is not, however, properly biaxial; the plane of the optic axes is sometimes parallel, sometimes perpendicular to the edge of the prism. Moreover this direction often changes from place to place in the same plate, and at times no bar is seen, but a black dot in the centre of the field surrounded by rings. Such behavior can be explained by supposing the crystal to be in a condition of internal strain. Sections parallel to the prism sometimes remain light between crossed nicols, sometimes extinguish at varying angles and

show a slight pleochroism, the absorption being $\epsilon > \omega$; the color a deep reddish orange.

In conclusion the author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice in connection with the present investigation, and to Prof. S. L. Penfield, under whose direction the crystallography of these salts was investigated. The author is also indebted to Mr. L. V. Pirsson for aid in the optical description of these salts.

SHEFFIELD SCIENTIFIC SCHOOL,
March, 1893.

ON SOME DOUBLE SALTS OF LEAD TETRACHLORIDE.*

By H. L. WELLS.

THE existence of lead tetrachloride has long been surmised from the fact that the corresponding oxide, when dissolved in cold hydrochloric acid, gives a yellow solution in which sulphuric acid does not give an immediate precipitate. Lead tetrachloride itself, however, has never been isolated, nor has any double salt which it forms been satisfactorily described.

Sobrero and Selmi † found that when chlorine is passed into a solution containing sodium chloride and lead chloride, the liquid becomes yellow. They found it impossible to isolate the compound either by evaporation or cooling, so that they determined the lead, sodium, and chlorine in such a solution, and found it to contain these constituents in the ratio corresponding to $PbCl_4 + 9NaCl$. Sobrero and Selmi say that perhaps this is the formula of the compound, but they put a question-mark after it. Their analysis indicates the existence of $PbCl_4$ in combination with NaCl, but if the solution had contained a compound of that composition, which was stable with water, it probably could have been isolated by evaporation. The fact is that the double salts of lead tetrachloride are not stable with water, as will be shown in the present article. Therefore, since a large excess of sodium chloride must have been present in the solution of Sobrero and Selmi, their analysis could not have determined the composition of the double salt that it contained.

Nicklès* saturated a strong solution of calcium chloride with lead chloride and chlorine and analyzed the *solution*. He

* Amer. Jour. Sci., xlvi, September, 1893.
† Ann. Chim. Phys., III, xxix, 161.
* Ibid., IV, x, 323.

found it to contain lead, calcium, and chlorine in the proportions represented by $PbCl_4 + 16CaCl_2$. In conclusion Nicklès does not claim that any such double salt exists, but merely claims to have indicated the existence of $PbCl_4$.

In view of the fact that the formulæ $PbCl_4 + 9NaCl$ and $PbCl_4 + 16CaCl_2$ merely represented the composition of solutions, it is remarkable that they are given in some handbooks of chemistry as real chemical compounds. It may be mentioned that Carnegie* has used the formula $PbCl_4.9NaCl$ in support of a theory on double halides.

O. Seidel † mentions unsuccessful attempts to isolate $PbCl_4$ and its double salts with the chlorides of other metals.

Fisher ‡ dissolved lead peroxide in hydrochloric acid, and found that all the lead in the solution was precipitated again as peroxide by the addition of sodium acetate. He was evidently not aware of the fact that Rivot, Beudant, and Daguin § had shown, long before, that lead is completely precipitated as peroxide by the addition of sodium acetate and chlorine to its solutions. Fisher found that two atoms of chlorine were used (as would be expected) in precipitating one atom of lead as peroxide. His conclusion that his experiments showed the existence of lead tetrachloride has, apparently, little foundation.

More recently, Ditte ‖ has made some experiments on the solubility of lead chloride in solutions containing hydrochloric acid and chlorine. He apparently does not believe in the existence of lead tetrachloride, for he does not mention the compound, while he explains the precipitation of lead peroxide, when such solutions are diluted, by saying that lead chloride is partly dissociated by the act of solution, that the solution then contains oxide of lead, and that this is peroxidized by the oxides of chlorine formed when chlorine is passed into the solution.

Nikolukine has succeeded in isolating double salts of lead tetrachloride with ammonium and potassium chlorides. He

* Am. Chem. Jour., xv, 10, 1893.
† Jour. pr. Ch., II, xx, 205, 1879.
‡ Jour. Chem. Soc., xxxv, 282, 1879.
§ Ann. Mines, V, iv, 239, 1853.
‖ Ann. Chim. Phys., V, xxii, 566, 1881.

showed that these compounds contain lead and extra chlorine in the proportion required for $PbCl_4$, but there is no evidence in the abstracts of his article * that he determined the composition of the double salts. His original article in Russian is not accessible to me. Nikolukine prepared the compounds by dissolving lead dioxide in concentrated hydrochloric acid in sealed tubes, and adding the alkaline chlorides to the solutions thus produced. He describes the double salts as having a lemon-yellow color, and states that they are pretty stable, the ammonium chloride compound being decomposed at 120°.

The present investigation has been undertaken with the view of determining the composition of the salts which Nikolukine discovered, and especially in order to investigate the corresponding rubidium and cæsium compounds, which, from analogy, were expected to be more insoluble and stable than the potassium salt. As a result, it has been found possible to prepare the whole series in a state of purity, and the expectations in regard to the easy preparation of the rubidium and cæsium salts have been fully realized. The following salts are to be described:

$(NH_4)_2PbCl_6$
K_2PbCl_6
Rb_2PbCl_6
Cs_2PbCl_6

These salts are all yellow, and they all crystallize in the isometric system with an octahedral habit.

These salts show a new relation between lead and other metals of Mendeléeff's group IV, with which this type is very common, especially among the double fluorides. It is to be noticed also that this type is almost invariable among the double salts which tetrahalides form, for platinum, iridium, osmium, and palladium give analogous, isomorphous compounds, while, as has been recently shown by Dr. H. L. Wheeler of this laboratory, tellurium gives an extensive series of octahedral salts of this type. The octahedral form of the

* Berichte, xviii, 370. 1885; Jour. Chem. Soc., i, 123.

anhydrous salts of this type is very characteristic, and it seems to be universal, except among the fluorides.

All of the lead salts to be described are decomposed by water with the formation of lead peroxide. Chlorine is usually set free at the same time. It may be assumed that two successive reactions take place, which may be represented by the following equations:

$$(1)\ PbCl_4 + 2H_2O = PbO_2 + 4HCl$$
$$(3)\ PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O$$

The extent to which the second reaction takes place depends upon the dilution and the temperature. If the amount of water present is not too great, a state of equilibrium is reached when a sufficient amount of alkaline chloride, hydrochloric acid, and chlorine have gone into solution, and the decomposition stops. The cæsium salt is more slowly decomposed by water than others. All the salts are decomposed by boiling with an excess of hydrochloric acid, but the decomposition of the cæsium compound is remarkably slow, especially in solutions containing much cæsium chloride.

When free chlorine is present the cæsium salt is almost completely insoluble in strong solutions of cæsium chloride and in hydrochloric acid. Although the rubidium salt is considerably more soluble, the difference is not great enough so that a quantitative separation can be made. It will be shown in the following article that cæsium can be approximately separated from potassium, sodium, and lithium by this means, and that when rubidium is also present the cæsium can be approximately determined indirectly.

The salts to be described can be washed with hydrochloric acid containing chlorine. They are perfectly stable on exposure to the air. When heated in capillary tubes, the ammonium salt begins to whiten at about 225°, the potassium salt at about 190°, and the cæsium and rubidium salts at about 280°. This temperature for the decomposition of the ammonium salt is about 100° higher than that given by Nikolukine. It is probable that difference is due to a typographical error.

Attempts were made to prepare corresponding sodium and calcium salts, without success.

In analyzing the salts, lead was separated and weighed as sulphate, and, in the filtrate from this, the alkali metal was determined as sulphate. To determine chlorine, a separate portion was decomposed by a solution of sodium arsenite and chlorine was determined in this as usual.

Ammonium-Plumbic Chloride, $(NH_4)_2PbCl_6$. — In preparing this salt, Nikolukine's method of using sealed tubes was found to be unnecessary. A solution of lead tetrachloride was made by adding slightly diluted hydrochloric acid to an excess of lead dioxide at 0°. This solution was quickly filtered through asbestos, and a saturated, cold solution of ammonium chloride in dilute hydrochloric acid was added until an abundant, yellow, crystalline precipitate was produced. The salt was pressed on paper, and then air-dried.

	Found.	Calculated for $(NH_4)_2PbCl_6$.
Ammonium		7.90
Lead	44.61	45.39
Chlorine	46.53	45.71

Potassium-Plumbic Chloride, K_2PbCl_6. — Chlorine was passed into a solution saturated with potassium chloride, lead chloride, and hydrochloric acid at 0°, without producing the double salt. Nikolukine has stated that the salt is soluble in an excess of potassium chloride, and, acting upon this suggestion, another solution was made, like the former except that no potassium chloride was used. On mixing about equal volumes of the two solutions and letting the mixture stand at 0° for several hours, a well-crystallized crop of the yellow double-salt was obtained. The air-dry salt was analyzed.

	Found.	Calculated for K_2PbCl_6.
Potassium	15.30	15.70
Lead	41.91	41.55
Chlorine	42.49	42.75
	99.70	100.00
Loss on heating	15.07	Cl_2 14.25

The above method of preparation gives a small yield, and it would probably be better to use a method analogous to that by which the ammonium salt was prepared.

Rubidium-Plumbic Chloride, Rb_2PbCl_6. — When 65 g. of rubidium chloride were dissolved in 250 c. c. of water with 4 g. of lead chloride, no precipitate was produced by saturating the solution with chlorine, but, on adding an equal volume of concentrated hydrochloric acid to this solution, an abundant, yellow, crystalline precipitate was produced. This was collected on a filter, washed with hydrochloric acid containing chlorine, and air-dried.

	Found.	Calculated for Rb_2PbCl_6.
Rubidium	28.62	28.93
Lead	34.98	35.03
Chlorine	35.85	36.03
	99.45	100.00
Loss on heating	12.41	Cl_2 12.01

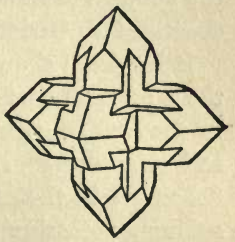
A solution 35 c. c. in volume, made of equal volumes of concentrated hydrochloric acid and water, and containing .0619 g. of rubidium and double the theoretical quantity of lead chloride, was saturated with chlorine. A precipitate of the double salt was produced, which, after standing several hours, was collected upon a Gooch filter. The rubidium in this precipitate was determined and found to amount to .0318 g. One cubic centimeter of the solution dissolved, therefore, .003 g. of the lead salt, equivalent to .00086 g. of rubidium. The experiment was made at about 20°.

Cæsium-Plumbic Chloride, $Cs\ PbCl_4$. — This salt is very readily prepared by passing chlorine into solutions containing lead chloride and a large excess of cæsium chloride. When hydrochloric acid is present, the excess of cæsium chloride is unnecessary, but in that case the precipitate is very finely divided. The precipitate begins to form in solutions that are nearly at a boiling temperature. A crop obtained without the use of hydrochloric acid was analyzed. It was washed with hydrochloric acid containing chlorine and air-dried.

	Found.		Calculated for Cs_2PbCl_6.
Cæsium	38.51		38.78
Lead	30.05		30.17
Chlorine	30.99		31.05
	99.55		100.00
Loss on heating . . .	10.96	Cl_2	10.35

The salt usually has a lemon-yellow color, but, when very strong hydrochloric acid is used and a large excess of lead chloride is present, the precipitate has a dark brown color. Such a crop gave the following analysis:

	Found.		Calculated for Cs_2PbCl_6.
Cæsium	38.19		38.78
Lead	29.64		30.17
Chlorine	31.35		31.05
	99.18		100.00
Loss on heating	11.09	Cl_2	10.35



This is evidently the same compound as the lemon-yellow salt. The cause of the brown color is not known. The presence of lead dioxide in it does not seem probable on account of the strong acid that was used, and, moreover, experiment showed that this oxide was instantly dissolved by the mother-liquor. It was suspected that this was a dimorphous form of the compound, but Mr. Louis V. Pirsson, who has kindly made a microscopic examination of both products, has found that both are isometric and octahedral in habit. He noticed that while the yellow salt forms perfect octahedrons, the brown compound occurs in octahedral groups composed of combinations of the cube and octahedron. The accompanying figure, by Mr. Pirsson, shows the prevailing habit of these crystals. The groups are very small, usually not over 0.015 mm. in diameter.

SHEFFIELD SCIENTIFIC SCHOOL,
March, 1893.

ON THE DOUBLE HALIDES OF ANTIMONY WITH RUBIDIUM.*

By H. L. WHEELER.

THE investigations of the double halides of antimony and rubidium have hitherto been confined to the chlorides, and the following salts have been described:

1 : 1	Rubidium	Antimony	Chloride,	$RbCl.SbCl_3$.
5 : 3	"	"	"	$5RbCl.3SbCl_3$
23 : 10	"	"	"	$23RbCl.10SbCl_3$
6 : 1	"	"	"	$6RbCl.SbCl_3$

The first three of these compounds were described by Remsen and Saunders.† These investigators, after a careful study of the subject, came to the conclusion that the salt $6RbCl.SbCl_3$ described by Godeffroy‡ does not exist.

It has been shown by the author of the present article that the 3 : 2 type of double salts is probably the only one formed by the combination of the arsenic halides with those of cæsium and rubidium.§ Moreover, since this type was observed by Schæffer‖ in the case of the double halides of antimony with sodium, potassium, and ammonium, and, since Remsen and Saunders obtained the salt $3CsCl.2SbCl_3$ it seemed probable that this type of double halides would exist with rubidium and antimony. A thorough re-examination of the chlorides has therefore been undertaken, and the investigation has been extended to the bromides and iodides. As a result of this investigation the following compounds have been obtained:

$RbCl.2SbCl_3.H_2O$	. . . . .	. . . . .
$RbCl.SbCl_3$.	. . . . .	. . . . .
$3RbCl.2SbCl_3$.	$3RbBr.2SbBr_3$	$3RbI.2SbI_3$
$23RbCl.10SbCl_3$ (?)	$23RbBr.10SbBr_3$ (?)	. . . . .

* Amer. Jour. Sci., xlvi, Oct., 1893.
† Amer. Chem. Jour., xiv, 155.
‡ Berichte, viii, 9.
§ Amer. Jour. Sci., xlvi, 88.
‖ Pogg. Ann., cix, 611.

The first chloride, $RbCl.2SbCl_3.H_2O$, is a new type of antimony rubidium halides, which Remsen and Saunders did not obtain. The second, 1 : 1, confirms the results of these investigators, while the series of 3 : 2 salts, which includes a chloride, bromide, and iodide, corresponds to the type expected from analogy. The difference between the percentage composition required for the 3 : 2 chloride and that required for the 5 : 3 formula of Remsen and Saunders is small, and it is to be noticed that these authors do not consider their formula as definitely established. They say, " The analytical results obtained from different samples varied considerably and it does not appear possible to obtain the salt in pure condition." It will be noticed that most of the analyses of the 3 : 2 chloride, made in the present investigation, show a composition intermediate between what is required for the formulas of the 3 : 2 and the 5 : 3 salts, but the bromide and the iodide were readily obtained in pure condition and gave analytical results closely corresponding to the 3 : 2 formula. Moreover the chloride, bromide, and iodide just mentioned are all hexagonal and may be referred to axes which correspond closely to those of the 3 : 2 arsenic compounds. The chloride and bromide with a complex composition (23 : 10 ?) confirm the results of Remsen and Saunders on the chloride. The formula suggested by them has been retained, subject to uncertainty. It will be seen beyond that, as Remsen and Saunders have noticed, the ratio 16 : 7 corresponds very closely to the analyses, and it may be added that the ratios 9 : 4 and 7 : 3 differ so little from the other two that it would be very difficult to distinguish between any of these ratios by analysis.

For the preparation of the double halides the constituents were mixed in the presence of the corresponding dilute acids. In the case of the chlorides a 10 per cent acid was used. The mixtures were then evaporated until crystals separated on cooling. Further details will be given with the descriptions of the salts. In the case of each salt several crops were prepared and analyzed, and an attempt has been made to determine approximately the limits of the conditions under

which these double halides are formed. It may be added that the analytical results are not selected, for with the exception of two antimony determinations, where an error had been detected, every determination that was made has been given.

Method of Analysis.

The salts were removed from the mother-liquor, and, after pressing on smooth filter paper, were dried in the air for a short time. Portions of a little less than half a gram were taken for analysis. In order to determine the halogens, silver nitrate was added to a solution of the substance in water containing a little tartaric and nitric acids, the mixture was then warmed on the water bath for a couple of hours, and finally, after standing twelve hours, the silver halide was collected, ignited, and weighed in a Gooch crucible in the usual manner. The determination of the antimony and rubidium was effected in a separate sample. In order to do this, the salts were dissolved in a little dilute hydrochloric acid and the solutions were diluted with boiling water. Hydrogen sulphide was then used to precipitate the antimony, and, when the solutions had cooled, the resulting sulphide was filtered on asbestos in a Gooch crucible, washed with water and alcohol and then heated to 230° in an oven filled with carbonic acid. On cooling, the sulphide was weighed as Sb_2S_3. The rubidium was determined by evaporating the filtrate from the antimony sulphide to dryness with an excess of sulphuric acid, the residue was then converted into normal sulphate by ignition in a stream of air containing ammonia. The atomic weights used in the calculation of results were the following:

Cl, 35.5; Br, 80; I, 127; Sb, 120; Rb, 85.5

The Double Chlorides.

The crystals of the double chlorides are colorless, with the exception of the salt $3RbCl.2SbCl_3$; this salt has a pale yellow color exactly similar to the salts $3RbCl.2AsCl_3$ and $3CsCl.2AsCl_3$. The stability of the double chlorides, on exposure,

appears to vary inversely with the quantity of antimony chloride which they contain.

1 : 2 Rubidium Antimony Chloride, $RbCl.2SbCl_3.H_2O$. — This new salt was obtained from hydrochloric acid solution when the constituents were mixed in the proportion of ten, eight, or six molecules of $SbCl_3$ to one of RbCl. On concentrating these mixtures supersaturated solutions were obtained which sometimes remained for days without giving crystals, but on shaking, or stirring with a glass rod, the crystallization was induced. The crystals separate in the form of elongated, colorless, monoclinic tables. Analysis of different crops gave:

	From Solutions of $10SbCl_3$ to 1RbCl.			From Solution of $8SbCl_3$ to 1RbCl.	From Solution of $6SbCl_3$ to 1RbCl.	Calculated for $RbCl.2SbCl_3.H_2O$.
Rb	14.61	14.71	14.74	14.64	15.07	14.44
Sb	40.75	40.97	41.09	41.07	40.97	40.54
Cl	41.83	41.53	41.11	. . .	. . .	41.98
H_2O	3.20	3.10	3.18	3.08	. . .	3.04

The crystals of this salt have a brilliant lustre when first removed from the mother-liquor, but on exposure they soon lose their lustre, becoming opaque and decomposing. In the preparation of this salt for analysis the crystals were crushed and thoroughly pressed on filter paper, and when it was certain that the powder did not contain any mechanically mixed water, it was placed in a weighing-tube. This salt is readily distinguished from the other colorless double halides of rubidium and antimony by the fact that it melts at 77°.

1 : 1 Rubidium Antimony Chloride, $RbCl.SbCl_3$. — This salt was first described by Remsen and Saunders; * they say that "if the excess of antimony chloride . . . be *very* great, a colorless salt crystallizing in elongated, apparently orthorhombic, crystals is obtained." I have found that by mixing the constituents in hydrochloric acid solutions, in the proportion of four or three molecules of $SbCl_3$ to one of RbCl, crystals of similar appearance were obtained. The solutions require a

* Loc. cit.

considerable degree of concentration, and the mother-liquor is more or less syrupy, hence the rubidium determinations came low and the antimony high. Analysis gave:

	From Solution of $4SbCl_3$ to 1RbCl.	From Solution of $3SbCl_3$ to 1RbCl.	Calculated for $RbCl.SbCl_3$.
Rb	23.67	23.96	24.61
Sb	35.38	34.99	34.53
Cl	40.70	40.73	40.86

A solution of antimony and rubidium chloride in the proportion of $2\frac{1}{2}$ molecules of the former to one of the latter gave a mixture of this salt and the yellow one described below. As has been observed by Remsen and Saunders, crystals of this salt rapidly lose their lustre on exposure. They give no definite melting-point below the temperature of boiling sulphuric acid.

3 : 2 Rubidium Antimony Chloride, $3RbCl.2SbCl_3$. — This is the salt to which Remsen and Saunders assign the formula $5RbCl.3SbCl_3$. They obtained this compound on adding "a considerable excess" of antimony chloride to a solution of the salt $23RbCl.10SbCl_3$. They describe the crystals as sometimes resembling a rhombohedron in general shape and having a pale yellow color, and they remark that "this is noteworthy, because the more complex salt ($23RbCl.10SbCl_3$) and the simpler one ($RbCl.SbCl_3$) are both colorless. It is to be remembered, however, that the salt $Cs_3Sb_2Cl_9$($3CsCl.2SbCl_3$) is also yellow." It may be added that both $3CsCl.2AsCl_3$ and $3RbCl.2AsCl_3$ are pale yellow. Remsen and Saunders also remark: "As the formula of this rubidium salt is not very simple, and as the substance could not be recrystallized, on account of the strong tendency towards the formation of the very complex salt, the formula suggested below can hardly be considered as definitely established."

I have found that when solutions of antimony chloride and rubidium chloride are mixed in the proportion of one and one-fifth molecules of the former to one molecule of the latter a pale yellow salt is obtained crystallizing in rhombohedra.

In one case, on obtaining a crop of crystals from a solution of $2SbCl_3$ to 1RbCl in strong HCl, the yellow rhombohedra were seen to be mixed with the colorless hexagonal plates, presumably of the salt $23RbCl.10SbCl_3$. It was also found that a wide difference exists in the solubility of these two salts in warm solutions; the yellow crystals dissolved with difficulty, while on the other hand the salt 23 : 10 went into solution with only a slight elevation of temperature. If the crystals of the yellow salt are warmed in the mother-liquor they become opaque throughout without losing their pale yellow color. It seems probable that impurities are dissolved out by this operation and that no decomposition takes place, for the decomposition products and the other double chlorides are colorless. An analysis of a crop obtained in this manner corresponded very closely to the formula $3RbCl.2SbCl_3$. Analysis gave:

	From Solutions of $2SbCl_3$ to 1RbCl.		From Solutions of $1\frac{1}{2}SbCl_3$ to 1RbCl.		From Solutions of $2SbCl_3$ to 1RbCl heated.	Calculated for $3RbCl.2SbCl_3$.	Calculated for $5RbCl.3SbCl_3$.
Rb	32.57	32.19	33.34	31.86	31.30	31.44	33.28
Sb	28.68	28.67	28.55	28.46	29.44	29.41	28.03
Cl	38.38	38.42	38.32	. . .	38.98	39.15	38.69

23 : 10? Rubidium Antimony Chloride, $23RbCl.10SbCl_3$. — For the preparation of this compound, a sample of rubidium chloride was used which had been specially purified for the purpose by the method recently described by Prof. H. L. Wells* of this laboratory. The purification of this sample was repeated after the product failed to give spectroscopic reactions for potassium and cæsium.

If solutions of antimony and rubidium chlorides are mixed in the proportion of one molecule of SbCl to one, four, or six molecules of RbCl, the crystals obtained are the "colorless six-sided plates, tables, or thicker crystals," to which Remsen and Saunders have assigned the formula $23RbCl.10SbCl_3$. The average results of the analyses of the different

* Amer. Jour. Sci., III, xlvi, 188.

crops of the double chloride gave figures closely agreeing with those of the above authors, but the ratio of rubidium to antimony came somewhat lower than theirs. Analysis gave:

	From Solution 6RbCl to 1$SbCl_3$.		From Solution 4RbCl to 1$SbCl_3$.	From Solution 1RbCl to 1$SbCl_3$.	Sample recrystallized from 10% HCl.	Average.	Ratio.
Rb	38.98	38.55	38.83	38.62	38.60	38.716	2.28
Sb	23.76		23.98	23.52	23.81	23.767	1.00
Cl	37.16	36.97	. . .	. . .	36.95	37.026	5.26

	Calculated for 23RbCl.10$SbCl_3$.	Calculated for 16RbCl.7$SbCl_3$.	Calculated for 9RbCl.4$SbCl_3$.	Calculated for 7RbCl.3$SbCl_3$.
Rb . .	38.96	38.85	38.57	39.21
Sb . .	23.77	23.86	24.06	23.58
Cl . .	37.27	37.29	37.37	37.21

It is to be noticed that this salt is formed under conditions varying more widely than in the case of any of the other double rubidium antimony chlorides. It can be exposed to the air for several days without losing its lustre; on long exposure it becomes covered with a white, opaque layer, probably of antimony oxychloride.

The Double Bromides.

The bromides were obtained in the form of brilliant yellow, six-sided plates, resembling the double arsenic bromides of rubidium and cæsium. They are comparatively stable in the air, but on long exposure the crystals lose their lustre.

3 : 2 Rubidium Antimony Bromide, *3RbBr.2SbBr*$_3$. —This salt was obtained from dilute hydrobromic acid solutions when the constituents were mixed in the proportion of two and three-tenths and also four molecules of RbBr to one of $SbBr_3$; it was also the only one formed when antimony bromide was present in the solutions in excess. It will be seen that a much larger range of conditions exists for the preparation of the salt $3RbBr.2SbBr_3$ than in the case of the corresponding double chloride. Moreover, the bromide can be recrystallized unaltered from dilute hydrobromic acid.

Analysis gave:

	From Solutions containing a large Excess of $SbBr_3$.		From Solution 23RbBr. to 10$SbBr_3$.	From Solution 4RbBr to 1$SbBr_3$.	Sample of Latter recrystallized from HBr.	Calculated. for 3RbBr. 2$SbBr_3$.
Rb . .	21.55	21.18	20.96	21.16	21.53	20.92	21.08
Sb . .	. . .	20.07	20.13	19.98	19.59	19.91	19.73
Br . .	59.30	. . .	. . .	. . .	. . .	59.07	59.19

23 : 10 (?) Rubidium Antimony Bromide, 23RbBr.10$SbBr_3$. — This salt was obtained when dilute hydrobromic acid solutions of rubidium and antimony bromides were mixed in the proportion of six, eight, and thirteen molecules of the former to one of the latter. The crystals obtained on slowly cooling these mixtures, with the exception of their strong yellow color, closely resemble the corresponding complex chloride. If the solutions are rapidly cooled the salt separates in the form of brilliant spangles. The average of the following results gives a remarkably close ratio to that required for the formula 23RbBr.10$SbBr_3$.

Analysis gave:

	From Solution 6RbBr to 1$SbBr_3$.	From Solution 8RbBr to 1$SbBr_3$.	From Solution 13RbBr to 1$SbBr_3$.			Sample of Latter recrystallized from conc. HBr.
Rb . .	26.66	26.16	26.92	26.60	26.71	26.39
Sb . .	16.11	16.23	16.18	16.26	16.22	16.18
Br . .	. . .	. . .	57.27	57.23	. . .	57.41

	Calculated for 23RbBr.10$SbBr_3$.	Calculated for 16RbBr.7$SbBr_3$.	Calculated for 9RbBr.4$SbBr_3$.	Calculated for 7RbBr.3$SbBr_3$.
Rb . .	26.55	26.47	26.27	26.74
Sb . .	16.20	16.25	16.38	16.08
Br . .	57.25	57.28	57.35	57.18

	Average of analytical Results.	Ratios derived			
Rb . .	26.57	.3107	or 23.03	or 16.12	or 9.21 or 6.90
Sb . .	16.19	.1349	" 10.00	" 7.00	" 4.00 " 3.00
Br . .	57.30	.7162	" 53.09	" 37.16	" 21.23 " 15.92

It is to be noticed that this salt is formed within a much smaller range of conditions than in the case of the chloride, and

can only be recrystallized from strong hydrobromic acid solutions. When recrystallized from moderately strong acid a mixture of the salts 23 : 10 and 3 : 2 was obtained, but from dilute acid a pure crop of the 3 : 2 compound separated.

	Recrystallized from strong HBr.	Recrystallized from dilute HBr.	Calculated for $3RbBr.2SbBr_3$.
Rb	25.54	21.89	21.08
Sb	16.93	19.70	19.73
Br	57.77	. . .	59.19

The Double Iodide.

3 : 2 Rubidium Antimony Iodide, $3RbI.2SbI_3$.— The formation of this salt was observed when a solution of rubidium iodide in hydriodic acid was saturated hot with antimony iodide; it was also obtained from a solution of antimony iodide in a large excess of rubidium iodide. The best crystals are obtained when a considerable quantity of antimony iodide is present; under these conditions large deep red lozenge-shaped crystals separate. Analysis gave:

	Large Excess of RbI.	Large Excess of SbI_3.	Calculated for $3RbI.2SbI_3$.
Rb	16.28	14.82	15.64
Sb	14.14	15.17	14.64
I	69.76	69.55	69.72

On exposure to the air the crystals slowly lose their lustre.

Crystallography.

The crystallization of the 3 : 2 double salts is hexagonal. In general the habit is rhombohedral and they can all be referred to axes of nearly equal length. The double bromide and iodide have a perfect basal cleavage, like the salts of the arsenic series, while the chloride gave only a conchoidal fracture. The axial ratios of the salts is shown by the following table, the ratios of the corresponding arsenic salts being given for comparison.

	$a : \dot{c}$		$a : c$		$a : \dot{c}$
$3RbCl.2SbCl_3$	1 : 1.125	$3RbCl.2AsCl_3$	1 : 1.210	$3CsCl.2AsCl_3$	1 : 1.209
$3RbBr.2SbBr_3$	1 : 1.207	$3RbBr.2AsBr_3$	1 : 1.220	$3CsBr.2AsBr_3$	1 : 1.219
$3RbI.2SbI_3$	1 : 1.230	$3RbI.2AsI_3$	1 : 1.242	$3CsI.2AsI_3$	1 : 1.244

From this table it may be seen that the substitution of arsenic by antimony produces little if any effect in the lengths of the axes, and in each series the vertical axes lengthen as the atomic weight of the halogen increases.

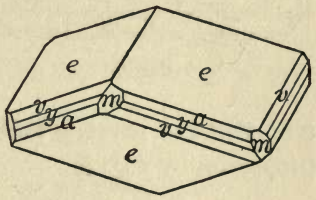


Fig. 1.

3Rb Cl.2Sb Cl₃. — This salt, unlike the others of the series, shows rhombohedral tetartohedrism. In one crop, where the crystals measured 5 to 7 mm. in diameter, the faces were developed on every crystal as in Fig. 1, the forms being

a, $11\bar{2}0$, *i*-2	*e*, $01\bar{1}2$, $-\frac{1}{2}$	*y*, $\bar{2}532$, $-\frac{1}{2}^{5}r$
m, $10\bar{1}0$, *I*	*v*, $\bar{1}3\bar{2}2$, $-\frac{1}{2}^{3}r$	

On a second crop only *e* and *a* were developed.

	Measured.	Calculated.
$e \wedge e$, $01\bar{1}2 \wedge 1\bar{1}02$	56° 18′	. . .
$e \wedge v$, $01\bar{1}2 \wedge \bar{1}3\bar{2}2$	29° 53′	29° 55′
$e \wedge y$, $\bar{1}3\bar{2}2 \wedge \bar{2}5\bar{3}2$	11° 29′	11° 26′
$y \wedge a$, $\bar{2}5\bar{3}2 \wedge \bar{1}2\bar{1}0$	20° 29′	20° 29′

This salt differs from all the others of the series, since it is the only one on which tetartohedrism has been observed. Whether the others are really tetartohedral, but have not shown it owing to the absence of highly modified forms, cannot be told at present. Also the basal cleavage, which is so prominent on all of the others, could not be detected, while the one-half rhombohedron *e* was only observed on this salt. A basal section was prepared, which in convergent polarized light showed a normal, uniaxial interference figure, the double refraction being negative, like the corresponding arsenic compound.

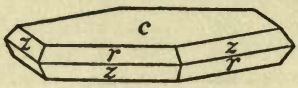


Fig. 2.

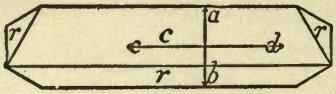


Fig. 3.

3RbBr.2SbBr$_3$. — Crystals of this salt were prepared up to 7 mm. in diameter. The habit is generally that of six-sided plates, Fig. 2, having the forms *c*, 0001, *O*; *r*, 10$\bar{1}$1, 1 and *z*, 01$\bar{1}$1, -1. In one crop *c*, *r*, and *m* were developed with some of the rhombohedral faces predominating to such an extent that the crystals looked like prisms, represented in basal projection by Fig. 3.

	Measured.	Calculated.
$r \wedge c$, 10$\bar{1}$1 $\wedge$ 0001	*52° 21′	. . .
$r \wedge z$, 10$\bar{1}$1 $\wedge$ 01$\bar{1}$1	48° 0′	47° 57′

None of the crystals show normal optical properties. Crystals like Fig. 3 showed for the most part an extinction parallel to the direction *c*–*d*, sometimes with twinned lamellæ prominent at one end. In convergent polarized light no interference figure was observed normal to *c*, but some of the crystals like Fig. 3 could be tilted up on a rhombohedron face and showed an acute bisectrix nearly normal to *r*. The axial angle was small and the dispersion strong, the optical axes being in the plane *a*–*b* for green and normal to that for red light, the interference figure looking like that of brookite.

3RbI.2SbI$_3$. — This salt, unlike the corresponding arsenic compound, was obtained in crystals of considerable size, some over 10 mm. in diameter. When prepared with an excess of SbI_3, usually lozenge-shaped crystals were obtained, shown in basal projection in Fig. 4. These were often grouped in twin position, penetration twins being prominent with a rhombohedron as twinning plane. From solutions containing an excess of RbI, the rhombohedral habit was observed, sometimes with a negative scalenohedron *s* 18.$\bar{9}$.17, $-\frac{7}{17}-\frac{2}{7}$, bevelling its pole edges, Fig. 5.

	Measured.	Calculated.
$m \wedge r$, $10\bar{1}0 \wedge 10\bar{1}1$	*35° 6′	. . .
$r \wedge c$, $10\bar{1}1 \wedge 0001$	54° 43′	48° 18′
$r \wedge z$, $10\bar{1}1 \wedge 01\bar{1}1$	47° 15′	48° 18′
$r \wedge r$, $10\bar{1}1 \wedge \bar{1}101$	89° 50′	90° 14′
$s \wedge s$, $18\bar{9}17 \wedge \bar{1}9\bar{8}17$	6° 40′	6° 21′

The basal cleavage was prominent, and sections parallel to this showed abnormal optical properties. Thin plates from the crystals like Fig. 4 showed middle and end sections with

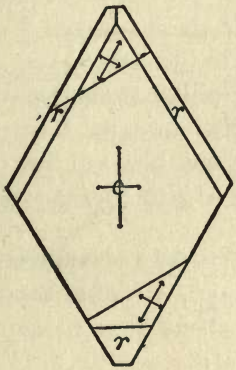


Fig. 4.

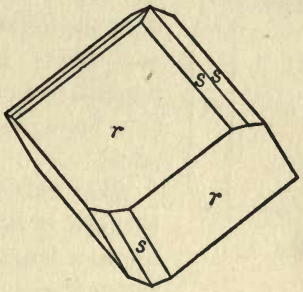


Fig. 5.

extinctions in the directions indicated by the arrows. In convergent light no interference figure was observed. This salt then, like $3RbBr.2SbBr_3$ and $3RbI.2AsI_3$, is only pseudo-hexagonal, being abnormal in its optical properties.

Rb Cl.Sb Cl$_3$. — The crystallization of this salt is monoclinic. Crystals were obtained 10 mm. long. The forms observed were

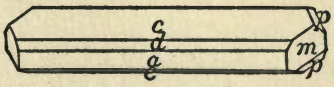


Fig. 6.

a, 100, *i*-$\bar{\imath}$	*m*, 110, *I*	*e*, $\bar{1}01$, 1-$\bar{\imath}$
c, 001, *O*	*d*, 101, $-$ 1-$\bar{\imath}$	*p*, $\bar{1}11$, 1

The habit is shown in Fig. 6. The axial ratio is $\dot{a} : b : \dot{c} = 1.732 : 1.000 : 1.085$; $\beta = 001 \wedge 100 = 65° 34'$.

	Measured.	Calculated.
$a \wedge c$, 100 ∧ 001	*65° 34′	. . .
$a \wedge m$, 100 ∧ 110	*57° 37′	. . .
$c \wedge e$, 001 ∧ $\bar{1}01$	*37° 36′	. . .
$m \wedge m$, 110 ∧ $\bar{1}10$	64° 46′	64° 46′
$a' \wedge e$, $\bar{1}00$ ∧ $\bar{1}01$	76° 54′	76° 50′
$p \wedge e$, $\bar{1}\bar{1}1$ ∧ $\bar{1}01$	46° 28′	46° 23′
$p \wedge c$, $\bar{1}\bar{1}1$ ∧ 001	56° 50′	56° 52′
$c \wedge d$, 001 ∧ 101	24° 21′	24° 22′
$d \wedge a$, 101 ∧ 100	41° 24′	41° 12′

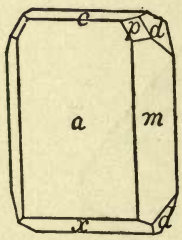


Fig. 7.

In polarized light these crystals show an extinction parallel to the ortho-axis. With crystals flattened parallel to the basal plane an obtuse bisectrix may be seen nearly normal to the base, the plane of the optical axis being at right angles to the symmetry plane.

$RbCl.2SbCl_3.H_2O$. — The crystallization of this salt is monoclinic. Crystals were made up to a length of about 9 or 10 mm. The forms observed were:

a, 100, i-$\bar{i}$		
c, 001, O	d, 021, 2-$\dot{i}$	p, 221, −2
m, 110, I	e, 011, 1-$\dot{i}$	x, $\bar{1}01$, 1-$\bar{i}$

The habit is shown in Fig. 7. The axial ratio is $\dot{a} : b : \dot{c}$ 1.699 : 1 : 0.820; $\beta = 001 \wedge 100 = 89° 28\frac{1}{2}'$.

	Measured.	Calculated.
$m \wedge m$, 110 ∧ $\bar{1}10$	*60° 57′	. . .
$a \wedge x$, 100 ∧ $\bar{1}01$	64° 49′	64° 40′
$m \wedge a$, 110 ∧ 100	59° 32′	59° 32′
$a \wedge c$, 100 ∧ 001	*89° 28½′	. . .
$x \wedge c$, $\bar{1}01$ ∧ 001	*25° 51½′	. . .
$c \wedge e$, 001 ∧ 011	39° 10′	39° 21′
$c \wedge d$, 001 ∧ 021	58° 20′	58° 37′
$a \wedge p$, 100 ∧ 221	63° 5′	63° 6′
$p \wedge d$, 221 ∧ 021	27° 5′	26° 37′

The crystals flattened parallel to the orthopinacoid show in polarized light an extinction parallel to the ortho-axis, and in convergent light a bisectrix and one of the ring systems appear near the limits of the field. The plane of the optical axis is the clinopinacoid.

The 23 : 10 bromide is pseudohexagonal. Basal plates always showed an intricate twinning when examined in polarized light. The pyramidal faces were horizontally striated and to such an extent that no satisfactory measurements could be made. In every respect this compound resembles the 23 : 10 chloride described by Remsen and Saunders.

In conclusion the author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice in connection with the present investigation and to Prof. S. L. Penfield, under whose generous supervision the crystallography of these salts was investigated.

SHEFFIELD SCIENTIFIC SCHOOL,
June, 1893.

ON THE DOUBLE CHLORIDES, BROMIDES, AND IODIDES OF CÆSIUM AND CADMIUM.*

By H. L. WELLS and P. T. WALDEN.

Since the cæsium-mercuric halides † had been studied by one of us with the result that six types of double salts were found, it seemed desirable to extend the investigation to the metal cadmium on account of its close relation to mercury. We have, therefore, undertaken this work, and as the result of a systematic and very thorough search have obtained the following compounds. The salt Cs_2CdCl_4 had already been described by Godeffroy.

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.
. . . .	Cs_2CdCl_4	$CsCdCl_3$
Cs_3CdBr_5	Cs_2CdBr_4	$CsCdBr_3$
Cs_3CdI_5	Cs_2CdI_4	$CsCdI_3.H_2O$

These cadmium salts correspond to the three types of mercuric compounds which contain the largest proportion of cæsium, and no evidence of the existence of cadmium double halides analogous to the 2 : 3, 1 : 2, and 1 : 5 types of cæsium-mercuric salts could be obtained. It is evident that the tendency to form a variety of double halides decreases from mercury to cadmium.

Three types of cadmium double halides with alkali metals and ammonium have been previously described, and a list of these is as follows:

4 : 1 Type.	2 : 1 Type.	1 : 1 Type.
$(NH_4)_4CdCl_6$	$(NH_4)_2CdCl_4.H_2O$	$KCdCl_3.\frac{1}{2}H_2O$
K_4CdCl_6	$Na_2CdCl_4.3H_2O$	$NaCdBr_3.2\frac{1}{2}H_2O$
$(NH_4)_4CdBr_6$	K_2CdCl_4	$KCdBr_3.\frac{1}{2}H_2O$
K_4CdBr_6	$K_2CdCl_4.H_2O$	$NH_4CdBr_3.\frac{1}{2}H_2O$
. . . . .	$(NH_4)_2CdI_4.2H_2O$	NH_4CdF_3
. . . . .	$Na_2CdI_4.6H_2O$	. . . . .
. . . . .	$K_2CdI_4.2H_2O$	. . . . .

* Amer. Jour. Sci., xlvi, December, 1893.

† Ibid., III, xliv, 221.

It is noticeable that, while the 2 : 1 and 1 : 1 salts in the above table correspond to two types of the cæsium salts which we have prepared, the 4 : 1 type of ammonium and potassium compounds differs from our 3 : 1 cæsium-cadmium salts and from the corresponding cæsium-mercuric compounds. We were entirely confident that our results were correct, for the salts were well crystallized and carefully prepared for analysis, and it was impossible to believe that we had obtained too little cæsium in our analyses, because the salts of this type were crystallized from solutions containing a large excess of cæsium halide. In order to convince ourselves that there was no mistake about the 4 : 1 formulæ we have prepared the two chlorides according to the directions of Von Hauer who described them. The salts were extremely well crystallized and it was easy to obtain them in a very pure condition. The results of the analyses were as follows:

	Found.		Calculated for K_4CdCl_6.
Potassium	32.35	. . .	32.49
Cadmium	23.39	23.36	23.27
Chlorine	44.00	44.12	44.24

	Found.		Calculated for $(NH_4)_4CdCl_6$.
Ammonium . . .	18.20	. . .	18.12
Cadmium	27.91	27.87	28.22
Chlorine	53.50	. . .	53.66

These results confirm Von Hauer's formulæ, and the curious fact must be accepted that cæsium forms 3 : 1 double halides with cadmium, while potassium and ammonium form salts of the 4 : 1 type.

The four types of cadmium double halides now known form a very simple and symmetrical series, the ratios of the alkali metal to cadmium being 4 : 1, 3 : 1, 2 : 1, and 1 : 1. The first two of these types do not conform to Remsen's so-called law * concerning the composition of double halides.

Preparation and General Properties. — The compounds to be described were prepared by making warm solutions of the

* Am. Chem. Jour., xi, 291.

component halides, and after concentrating if necessary, cooling to crystallization. Water, slightly acidified with the corresponding acid to prevent the formation of basic compounds, was used as the solvent, and in one instance, where a solution became syrupy from a large excess of a cadmium salt, alcohol was also tried, but without any advantage. The conditions were varied gradually in each case all the way from the point where the solution was saturated with the cæsium halide to the point where it was saturated with the cadmium halide, and so many experiments were made that we believe that no double salt, capable of existence at the temperatures used, was overlooked. It was noticed that variations in the concentration of any given solution had little effect upon the identity of the salt produced. In this respect the cadmium compounds differ considerably from those of mercury, for with the latter concentration is often an important factor in determining the salt produced.

The three 1 : 1 compounds $CsCdCl_3$, $CsCdBr_3$, and $CsCdI_3 . H_2O$ and also the 2 : 1 iodide Cs_2CdI_4 are capable of being recrystallized from water unchanged. The salt Cs_2CdCl_4, when dissolved in water, yields $CsCdCl_3$, the two bromides Cs_3CdBr_5 and Cs_2CdBr_4 yield $CsCdBr_3$, while the iodide Cs_3CdI_5 gives Cs_2CdI_4. These facts show that the salts having the larger proportions of cæsium require the presence of an excess of cæsium halide for their formation. The 1 : 1 salts all crystallize unchanged from extremely concentrated solutions of the corresponding cadmium halides.

All the salts are colorless. A pale violet color noticed in a few crops of the bromide Cs_2CdBr_4 is supposed to have been due to some unknown foreign substance.

The solubility of the analogous salts in water or in saline solutions evidently increases from the chlorides to the iodides. The iodides consequently yield the largest crystals, while the chlorides give the smallest.

Methods of Analysis. — The products were carefully examined, and nothing was analyzed that was not homogeneous. The crystals, which, in several instances, were large and fine

and in no case hygroscopic, were freed from mother-liquor with great care by pressing and crushing them on smooth filter-paper. They were then simply air-dried for analysis.

Cadmium was precipitated as sulphide, this was dissolved in hydrochloric acid containing bromine, and after the free acid had been removed by evaporation, the cadmium was precipitated with potassium carbonate solution, and cadmium oxide was weighed on a Gooch filter. The cæsium in the filtrate from the cadmium sulphide was determined as normal sulphate. The halogens were determined in separate portions by the usual gravimetric method.

In every case at least two separate crops of a salt were made and analyzed, so as to avoid any chance of mistakes arising from mixtures.

2 : 1 Cæsium-Cadmium Chloride, Cs_2CdCl_4. — This salt is produced as a precipitate when a solution of cadmium chloride is added to a concentrated cæsium chloride solution. The precipitate dissolves upon warming the liquid, and crystallizes out in very small, rectangular plates when the solution is cooled. Its formation was observed when 50 g. of cæsium chloride and 3 g. of cadmium chloride were used, and it continued to be produced with the same amount of cæsium chloride until the amount of cadmium chloride had been increased to 18 g., at which point the 1 : 1 salt began to form. The salt is very sparingly soluble in cæsium chloride solutions, and it is probably due to this fact that no chloride of the 3 : 1 type could be obtained.

Three separate crops gave the following results on analysis:

	Found.			Calculated for Cs_2CdCl_4.
Cæsium . . .	51.55	51.26	51.51	51.35
Cadmium . .	21.45	21.50	. . .	21.62
Chlorine . .	27.03	27.14	26.90	27.03
	100.03	99.90		100.00

1 : 1 Cæsium-Cadmium Chloride, $CsCdCl_3$. — This was obtained only as a white crystalline powder. It is formed under

a very wide range of conditions, being produced by the recrystallization of the preceding salt, and continuing to appear until the solution is saturated with cadmium chloride. It is very difficultly soluble, especially in concentrated cadmium chloride solutions, and it can be recrystallized unaltered from water. Two samples, obtained under widely different conditions, were analyzed.

	Found.		Calculated for $CsCdCl_3$.
Cæsium	38.11	37.60	37.84
Cadmium . . .	31.80	31.97	31.86
Chlorine . . .	30.17	30.25	30.30
	100.08	99.82	100.00

3 : 1 Cæsium-Cadmium Bromide, Cs_3CdBr_5. — This compound was obtained in the form of rectangular plates, sometimes as much as 10 mm. in diameter. It can be made from a solution of 80 g. of cæsium bromide and 4.5 g. of cadmium bromide in sufficient water to make a volume of 120 c. c. On recrystallization it gives $CsCdBr_3$.

Two separate samples were analyzed.

	Found.		Calculated for Cs_3CdBr_5.
Cæsium . . .	44.25	44.27	43.80
Cadmium . . .	11.88	. . .	12.29
Bromine . . .	43.79	43.77	43.91
	99.92		100.00

2 : 1 Cæsium-Cadmium Bromide, Cs_2CdBr_4. — This was obtained in the form of slender needles, usually colorless, but sometimes possessing a pale violet color for some unknown reason. A solution 120 c. c. in volume, containing 3 g. of cadmium bromide and 52 g. of cæsium bromide gave this salt. When recrystallized from water, it gives, like the preceding salt, the compound $CsCdBr_3$.

The following analyses of separate crops were made. No. IV was a simple of the pale violet variety.

	Found.				Calculated for Cs_2CdBr_4.
	I.	II.	III.	IV.	
Cs . . .	40.46	40.53	. . .	40.46	38.11
Cd . . .	14.55	14.62	14.68	14.78	16.05
Br . . .	45.12	44.97	45.04	45.04	45.84
	100.13	100.12		100.28	100.00

Although the analyses agree well among themselves, it is noticeable that they vary considerably from the calculated composition. This disagreement is probably due to contamination with cæsium chloride, resulting from the large surface exposed by the slender crystals and the concentration of the mother-liquor. Moreover, analogy with the chloride and iodide makes the simple formula Cs_2CdBr_4 far more probable than the complicated formula $Cs_7Cd_3Br_{13}$ with which the analyses correspond.

1 : 1 Cæsium-Cadmium Bromide, $CsCdBr_3$. — The conditions under which this compound is formed are very wide in range, for it is produced by recrystallizing Cs_3CdBr_5, and it continues to appear as cadmium bromide is added until the solution is saturated with this very soluble salt.

The compound is evidently dimorphous. One form occurs as a crystalline precipitate, apparently isometric in form, under narrow limits of conditions when cæsium bromide is in excess, being produced when Cs_3CdBr_5 is recrystallized from water. The other form occurs in well-crystallized prisms, and is obtained when Cs_2CdBr_4 is recrystallized and when cadmium bromide is in excess of this proportion. It is interesting to notice that we have described a cæsium-lead bromide * of this type, $CsPbBr_3$, which is dimorphous, and that one of us has described the dimorphous mercuric compounds,† $CsHgCl_3$ and $CsHgBr_3$, which also belong to the same type.

Below are the analyses of four separate samples. Number IV is the granular, isometric salt; the others represent the prismatic compound.

* Amer. Jour. Sci., xlv, 128.

† Ibid., xliv, 225 and 228.

	Found.				Calculated for $CsCdBr_3$.
	I.	II.	III.	IV.	
Cs . . .	27.67	27.48	. . .	27.95	27.42
Cd . . .	22.97	23.08	22.87	22.92	23.09
Br . . .	49.49	49.42	49.33	49.30	49.49
	100.13	99.98		100.17	100.00

3 : 1 Cæsium-Cadmium Iodide, Cs_3CdI_5. — This salt crystallizes beautifully in large, stout, twinned prisms which show a variety of habits. Some of the crystals obtained were as much as 50 mm. in diameter. Its formation was observed when 182 g. of cæsium iodide and 65 g. of cadmium iodide were dissolved in sufficient water to make a volume of 200 c. c.

Four crops gave the following results on analysis:

	Found.				Calculated for Cs_3CdI_5.
Cs . . .	34.85	34.89	34.78	. . .	34.82
Cd . . .	9.78	9.79	9.84	9.55	9.77
I . . .	55.23	55.35	55.32	55.36	55.41
	99.86	100.03	99.94		100.00

2 : 1 Cæsium-Cadmium Iodide, Cs_2CdI_4. — This, like the corresponding mercuric salt, crystallizes in nearly square plates, in prisms, and in intermediate forms. Some of the plates obtained were 50 or 75 mm. in diameter. It can be prepared by recrystallizing Cs_3CdI_5 from water, and as the proportion of cadmium iodide is increased, it continues to form until the ratio of cadmium to cæsium has almost reached 1 : 1. The range of its formation is, therefore, much greater than that of the corresponding chloride and bromide, and it also differs from these in being recrystallizable from water. Three different samples were analyzed.

	Found.			Calculated for Cs_3CdI_4.
Cæsium . . .	29.85	30.29	30.23	30.03
Cadmium . .	12.56	12.53	12.46	12.64
Iodine		57.27	57.42	57.33
		100.09	100.11	100.00

1 : 1 Cæsium-Cadmium Iodide, $CsCdI_3.H_2O$. — This salt forms thin plates, often 20 to 30 mm. in diameter. It is the

only hydrous cæsium-cadmium halide that we have obtained, and it is stable when exposed to the air at ordinary temperatures.

It was considered doubtful whether the corresponding cæsium mercuric iodide * contained a molecule of feebly combined water or not, but since both the cadmium and mercuric salts crystallize in thin plates, it is now believed, from analogy, that the mercuric compound was really hydrous.

The compound under consideration is formed under wide limits of conditions when the cadmium present is atomically equivalent to or in excess of the cæsium. It can be recrystallized from water. The samples analyzed were prepared under widely varying conditions.

	Found.			Calculated for $CsCdI_3.H_2O$.
Cæsium	20.89	20.75	. . .	20.66
Cadmium . . .	17.13	17.43	17.89	17.39
Iodine	59.21	59.18	. . .	59.16
Water	2.88	2.80	2.76	2.79
	100.11	100.16		100.00

SHEFFIELD SCIENTIFIC SCHOOL,
August, 1893.

* Amer. Jour. Sci., xliv, 230.

ON THE DOUBLE CHLORIDES, BROMIDES, AND IODIDES OF CÆSIUM AND ZINC, AND OF CÆSIUM AND MAGNESIUM.*

By H. L. WELLS and G. F. CAMPBELL.

The cæsium-mercuric and the cæsium-cadmium halides have already been studied in this laboratory, and it has seemed desirable to extend the investigation to the zinc and magnesium compounds, thus completing the study of the cæsium double halides of this family of bivalent metals as far as the chlorides, bromides, and iodides are concerned.

We have obtained the following salts;

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.
Cs_3ZnCl_5	Cs_2ZnCl_4	?
Cs_3ZnBr_5	Cs_2ZnBr_4	?
Cs_3ZnI_5	Cs_2ZnI_4	?
. . . .	. . . .	$CsMgCl_3.6H_2O$
. . . .	. . . .	$CsMgBr_3.6H_2O$
. . . .	. . . .	. . . . .

A systematic and thorough search has been made in all cases, and it is remarkable that while mercury gave six types of cæsium double salts and cadmium gave three, only two could be obtained with zinc and one with magnesium. It is evident that the variety of these double salts increases with the atomic weight of the bivalent metal. The existence of zinc salts of the 1 : 1 type is suspected, but the suspected products were obtained only in extremely concentrated zinc halide solutions of such a syrupy nature that no satisfactory analyses of them could be made.

The previously described double halides of zinc and magnesium with the alkali metals, as far as we have been able to find them, are given in the following table:

* Amer. Jour. Sci., xlvi, December, 1893.

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.
$(NH_4)_3ZnCl_5$	$(NH_4)_2ZnCl_4$	$NH_4ZnCl_3.2H_3O$
. . . . .	$(NH_4)_2ZnCl_4.H_2O$	$KZnI_3$
. . . . .	$Na_2ZnCl_4.3H_2O$	$NaZnI_3.1\frac{1}{2}H_2O$
. . . . .	K_2ZnCl_4	$NaZnF_3$
. . . . .	$(NH_4)_2ZnBr_4$	$KZnF_3$
. . . . .	$(NH_4)_2ZnI_4$	$NH_4MgCl_3.6H_2O$
. . . . .	$Na_2ZnI_4.3H_2O$	$NaMgCl_3.H_2O$
. . . . .	K_2ZnI_4	$KMgCl_3.6H_2O$
. . . . .	K_2ZnF_4	$RbMgCl_3.6H_2O$
. . . . .	$(NH_4)_2ZnF_4.2H_2O$	$NH_4MgBr_3.6H_2O$
. . . . .	. . . . .	$KMgBr_3.6H_2O$
. . . . .	. . . . .	$NH_4MgI_3.6H_2O$
. . . . .	. . . . .	$KMgI_3.6H_2O$
. . . . .	. . . . .	$NaMgF_3$

There is but a single 3 : 1 salt, corresponding to our new cæsium compounds of that type. This was described by Marignac. A few 1 : 1 zinc salts have been described, hence it is remarkable that cæsium zinc salts of this type could not be obtained in a pure condition, for previous experience in this laboratory has shown that cæsium usually forms less soluble and more stable double halides than the other alkali metals. All the previously described magnesium salts belong to the 1 : 1 type * to which our cæsium salts belong, and like the latter nearly all have six molecules of water.

The cæsium-magnesium bromide is formed under narrower limits of conditions than the chloride, while no iodide could be prepared, for cæsium iodide crystallized unchanged from syrupy solutions of magnesium iodide. This behavior was quite unexpected in view of the fact that the ammonium and potassium double iodides are known, and we have here another instance where cæsium, in spite of its usual tendency to form double salts, is inferior in this respect to other alkali metals. The idea suggests itself that great differences between the

* Lerch has shown (J. Pr. Ch., II, xxviii, 338) that the salts $2KBr.MgBr_2.6H_2O$ and $2NH_4Br.MgBr_2.6H_2O$ of Löwig do not exist.

atomic weights of the alkali-metal and the less positive metal are unfavorable for the formation of double salts, but more facts will be necessary in order to establish such a rule.

The cæsium-magnesium salts show an increase in ease of formation from the iodide to the chloride. Such a gradation, both in variety of salts and ease of preparation, is evident in a number of series of double halides which have been studied in this laboratory, and the well-known tendency of fluorides to form double salts indicates that the gradation probably extends to these compounds.

3 : 1 Cæsium-Zinc Chloride, Bromide, and Iodide, Cs_3ZnCl_5, Cs_3ZnBr_5, and Cs_3ZnI_5. — Each of these salts crystallizes in colorless prisms, apparently monoclinic in form. They are produced by making aqueous solutions of the constituents in the calculated proportions, but in the case of the iodide, with these proportions the 2 : 1 salt may form if the solution is too dilute. The salts under consideration continue to form as the relative amounts of cæsium halides are increased until the latter crystallize upon them. This indicates that no double salts with a higher proportion of cæsium exist. The iodide forms under rather wider limits of conditions than the other two salts, and it usually forms larger crystals. All the salts require concentrated cæsium halide solutions for their preparation, and the chloride especially is difficult to obtain in sufficient quantity for analysis unless as much as one or two hundred grams of the cæsium halide is used. The following analyses were made, all of which represent separate crops :

	Found.		Calculated for Cs_3ZnCl_5.
Cæsium	62.46	. . .	62.20
Zinc	10.08	9.80	10.13
Chlorine	27.43	27.34	27.67

	Found.			Calculated for Cs_3ZnBr_5.
Cæsium	47.12	. . .	. . .	46.18
Zinc	7.32	7.54	7.87	7.52
Bromine . . .	45.91	46.54	45.85	46.30

	Found.			Calculated for Cs_2ZnI_2.
Cæsium	36.54	36.20	36.08	36.30
Zinc	5.77	5.95	5.74	5.92
Iodine	56.89	57.16	. . .	57.78

2 : 1 Cæsium-Zinc Chloride, Bromide and Iodide, Cs_2ZnCl_4, Cs_2ZnBr_4, and Cs_2ZnI_4. — These salts form colorless plates, decreasing in size from the iodide to the chloride. They are all readily produced when larger proportions of the zinc halides are used than are necessary for the 3 : 1 compounds, and they recrystallize from water unchanged. They continue to form, through a wide range of conditions, as more of the zinc halides are added until the solutions become syrupy. In extremely syrupy solutions crystals of a different appearance were noticed, but on account of the nature of these solutions, no satisfactory analyses of these products could be made. It seems probable that they were 1 : 1 salts, analogous to the cadmium salts of that type.

The following analyses of separate crops were made:

	Found.		Calculated for Cs_2ZnCl_4.
Cæsium	55.97	56.09	56.26
Zinc	13.49	13.87	13.72
Chlorine	29.89	29.97	30.02

	Found.		Calculated for Cs_2ZnBr_4.
Cæsium	40.68	. . .	40.86
Zinc	9.53	9.72	9.98
Bromine	49.30	49.17	49.16

	Found.		Calculated for Cs_2ZnI_4.
Cæsium	31.49	31.55	31.70
Zinc	7.61	7.82	7.75
Iodine	60.43	. . .	60.55

Cæsium-Magnesium Chloride and Bromide, $CsMgCl_3.6H_2O$ and $CsMgBr_3.6H_2O$. — These salts form colorless, rectangular plates or flat prisms which are often striated. A thorough search gave no indications of salts of other types. The

chloride is formed under a wide range of conditions, the bromide under a much narrower range, while no double iodide at all could be prepared.

The following analyses were made of separate products:

	Found.				Calculated for $CsMgCl_3.6H_2O$.
Cs . . .	37.14	. . .	35.66	. . .	35.77
Mg . . .	6.80	. . .	. . .	6.83	6.53
Cl . . .	29.84	30.13	29.70	29.55	28.65
H_2O . .	. . .	30.93	. . .	. . .	29.05

	Found.			Calculated for $CsMgBr_3.6H_2O$.
Cs	27.23	27.67	. . .	26.32
Mg	4.96	4.50	5.07	4.81
Br	48.93	48.65	. . .	47.51
H_2O	18.32	. . .	22.33	21.37

It should be mentioned that Dr. H. L. Wheeler of this laboratory has attempted to prepare a double chloride of cæsium and beryllium. He found that the simple salts crystallized side by side from sufficiently concentrated solutions, and there were no indications of the existence of any double salt, even at rather low temperatures. It is therefore evident that beryllium follows the rule, already indicated, that in this family of bivalent elements, Be, Mg, Zn, Cd, Hg, the tendency to form double halogen salts increases with their atomic weights.

SHEFFIELD SCIENTIFIC SCHOOL,
August, 1893.

ON THE CÆSIUM-CUPRIC CHLORIDES.*

By H. L. WELLS and L. C. DUPEE.

As a continuation of the work done in this laboratory on double halogen salts, we have taken up the cæsium-cupric chlorides, which had never been thoroughly investigated. The result has been the discovery of four double salts belonging to three different types. The beauty of the crystals in size and form, and the magnificent and unexpected colors of some of them have made the investigation a very interesting one. The colors of the anhydrous salts, yellow and red, were perhaps not very remarkable since anhydrous cupric chloride is reddish brown, but since water of crystallization is supposed to give green and blue colors to cupric salts, we were considerably surprised to find that a brown salt, $Cs_3Cu_2Cl_7.2H_2O$, was hydrous. The color of this hydrous salt is, however, not without analogy, for a garnet-red, hydrous lithium-cupric chloride is known, $LiCuCl_2.2\frac{1}{2}H_2O$ according to Chassevant,† or $LiCuCl_3.2H_2O$ according to Meyerhoffer ; ‡ moreover Engel has described § a garnet-red compound $HCuCl_3.3H_2O$, and Sabatier's red salt $H_2CuCl_4.5H_2O$,‖ is similarly exceptional in color.

In this connection it should be noticed that cupric chloride, when dissolved in water with an excess of cæsium chloride, gives a bright yellow solution when it is hot and concentrated. It is well known that solutions of cupric chloride in concentrated hydrochloric acid have the same yellow color.

A list of the formulæ of the salts to be described, with their colors, is given below. The first salt has already been described by Godeffroy.¶

* Amer. Jour. Sci., xlvii, Feb. 1894.
† Compt. rend., cxiii, 646.
‡ Monatshefte, xiii, 716.
§ Compt. rend., cvi, 273.
‖ Ibid., cvi, 1724.
¶ Berichte, viii, 9.

Cs_2CuCl_4	Brilliant yellow.
$Cs_2CuCl_4.2H_2O$	Bluish green.
$Cs_3Cu_2Cl_7.2H_2O$	Brown.
$CsCuCl_3$	Garnet-red.

The previously described cupric double halides containing alkali metals and ammonium belong to two of the types which we have found in investigating the cæsium-cupric chlorides. A list of all those that we have been able to find is given below. Four of the double fluorides have been recently described by Von Helmont.*

2 : 1 Type.	1 : 1 Type.
$(NH_4)_2CuCl_4.2H_2O$	$NH_4CuCl_3.2H_2O$
$K_2CuCl_4.2H_2O$	$NH_4CuF_3.2\frac{1}{2}H_2O$
K_2CuF_4	$KCuF_3$
$(NH_4)_2CuF_4.2H_2O$	$RbCuF_3$
. . . . .	$LiCuCl_3.2H_2O$

It is to be noticed that this list contains salts which correspond exactly to three of the cæsium compounds, and that the group of 2 : 1 salts with two molecules of water is a conspicuous one.

The salt $Cs_3Cu_2Cl_7.2H_2O$ is an interesting one because it is apparently the only known double halide of an alkali metal with a bivalent metal, which has the 3 : 2 ratio.

The cæsium salts were investigated systematically by starting with a solution of 50 g. of cæsium chloride and adding to this from 3 to 5 g. of cupric chloride at a time, evaporating after each addition and observing the products. At the same time another series of experiments was made by beginning with a solution of 50 g. of cupric chloride, adding cæsium chloride to this gradually and operating in the same manner as in the other case. Many additional experiments were made, sometimes with the use of as much as 200 g. of cæsium chloride, and a number of crystallizations were made in the presence of hydrochloric acid of various strengths. It is believed

* Zeitschr. anorg. Chem., iii, 115.

that no double salt capable of existence either in warm solutions or at ordinary temperatures has been overlooked.

The salts were so well crystallized and so distinct in form and color that there was no difficulty in selecting pure products for analysis. The usual precautions, often mentioned in communications from this laboratory, were taken for the removal of mother-liquor from the crystals.

In analyzing the salts copper and cæsium were determined in one portion, the first as subsulphide, the other as normal sulphate. The chlorine was determined in separate portions, by the usual gravimetric method.

Anhydrous 2 : 1 Cæsium-Cupric Chloride, Cs_2CuCl_2. — This salt, which Godeffroy first described, forms magnificent, yellow, orthorhombic prisms, which were often obtained several centimeters in length and several millimeters in thickness. The crystals are usually attached at one end, and they often arrange themselves in parallel position, forming flat clusters. Doubly terminated, short crystals were occasionally observed. Its formation was observed, with 50 g. of cæsium chloride, in the presence of from 5 to about 25 g. of cupric chloride. It can be recrystallized from water if the solution is made so concentrated that crystals form on cooling, but with more dilute solutions one or both of the hydrous salts are usually deposited on standing or on spontaneous evaporation. The following analyses represent different crops made under considerable differences of conditions:

		Found.			Calculated for Cs_2CuCl_4.
Cs . . .	. . .	56.33	56.14	56.18	56.42
Cu . . .	13.52	13.45	13.47	13.48	13.46
Cl . . .	30.07	29.99	30.04	30.03	30.12
		99.77	99.65	99.69	100.00

Hydrous 2 : 1 Cæsium-Cupric Chloride, $Cs_2CuCl_4.2H_2O$. — This salt is bluish green in color, and it loses its water very rapidly on exposure to the air with a change of color to bright yellow. It is a well-crystallized, transparent salt, but its form was not made out on account of its instability. It is difficult

to prepare it, at least at summer temperatures under which this investigation has been made, and we have only occasionally observed it. It is formed by allowing solutions containing nearly the required proportions of cæsium and copper chlorides to evaporate spontaneously. A sample quickly pressed on paper gave the following analysis:

	Found.	Calculated for $Cs_2CuCl_4.2H_2O$.
Cæsium	51.28	52.40
Copper	12.53	12.50
Chlorine	. . .	28.00
Water	7.20	7.10

Another sample, which had been exposed to the air too long, gave 6.02 per cent of water, and the dehydrated compound gave the following analysis:

	Found.	Calculated.
Cæsium	56.09	56.42
Copper	13.68	13.46

3 : 2 Cæsium-Cupric Chloride, $Cs_3Cu_2Cl_7.2H_2O$. — This compound was obtained from solutions of nearly the required proportions of cæsium and cupric chlorides. It usually forms only at ordinary temperatures, and if the solution is too concentrated, one or both of the anhydrous salts will be deposited while it is warm. The salt forms triclinic crystals, often one or two centimeters in diameter. The large crystals are deep brown in color, small ones and fragments are very much paler, while the powder is yellow. It is nearly stable at ordinary temperatures, but gradually loses its lustre on long exposure. All the water goes off readily at 100°. The following analyses of separate crops were made:

	Found.			Calculated for $Cs_3Cu_2Cl_7.2H_2O$.
Cæsium		49.36	48.96	49.23
Copper . .	15.68	15.90	15.74	15.67
Chlorine . .	30.84	29.90	30.69	30.66
Water . . .	4.22	4.38	4.41	4.44
		99.54	99.80	100.00

1 : 1 Cæsium-Cupric Chloride, $CsCuCl_3$. — This is formed under wide variations of conditions, up to the point where the solution is saturated with cupric chloride. It can be recrystallized from water. It forms slender hexagonal prisms terminated by pyramids. The color is a deep garnet-red, and all except very slender crystals appear black by reflected light. The following analyses of separate products were made:

	Found.			Calculated for $CsCuCl_3$.
Cæsium . . .	43.67	. . .	43.58	43.89
Copper . . .	21.16	21.17	21.06	20.96
Chlorine . .	35.25	35.22	35.00	35.15
	100.08		99.64	100.00

SHEFFIELD SCIENTIFIC SCHOOL,
September, 1893.

ON THE CÆSIUM-CUPRIC BROMIDES.*

By H. L. WELLS and P. T. WALDEN.

We have made a systematic investigation of the cæsium-cupric bromides, following the plan, described in the preceding article, which was used for the corresponding chlorides. Although the work has been very thorough, we have found only the following two salts:

$$Cs_2CuBr_4 \text{ and } CsCuBr_3.$$

These salts correspond to the two common types of cupric double halides. The fact that no hydrous salts could be obtained was unexpected, because it has been pointed out by Remsen † in the case of certain double halides, and it has been observed by one of us in the case of the alkaline-lead halides, ‡ that the tendency to combine with water seems to increase with the atomic weight of the halogen. The fact that hydrous double chlorides of cæsium and copper exist, while no corresponding bromides were obtained indicates that the rule does not apply in all cases.

2 : 1 Cæsium-Cupric Bromide, Cs_2CuBr_4. — This compound forms opaque, black crystals having a greenish tint. The powder is black. In form and habit it resembles the corresponding chloride and is evidently orthorhombic like that salt. Elongated prisms, usually not over 5 to 10 mm. in length, commonly occurring in groups in parallel position, were observed where an excess of cæsium bromide was used. When the proportion of cupric bromide was increased, small short crystals made their appearance.

With 50 g. of cæsium bromide the compound is formed in the presence of from 5 to about 70 g. of cupric bromide. The

* Amer. Jour. Sci., xlvii, February, 1894.

† Amer. Chem. Jour., xiv, 88. ‡ Amer. Jour. Sci., xlvi, 37.

range of conditions under which it is formed are considerably wider than in the case of the corresponding chloride.

Of the analyses given below, A, B, C, D, and E represent a series of preparations in which copper bromide was gradually increased from 5 g. in A to 46 g. in E, while the cæsium bromide remained constant at about 50 g. and the volume increased from 100 c. c. in A to 150 c. c. in E. The sample F was obtained by recrystallizing the salt from water, while G resulted from recrystallizing $CsCuBr_3$.

	Cs.	Cu.	Br.	
A	40.80	9.46	49.38 =	99.64
B	. . .	9.68	. . .	. . .
C	40.75	9.74	48.97 =	99.46
D	40.88	9.69	48.95 =	99.52
E	. . .	9.78	49.40	. . .
F	41.11	9.66	. . .	. . .
G	. . .	10.00	. . .	. . .
Calculated for Cs_2CuBr_4	40.96	9.77	49.27 =	100.00

1 : 1 Cæsium-Cupric Bromide $CsCuBr_3$. — This salt forms short, hexagonal crystals which are strung together end to end. They are dark and opaque, giving a bronze-colored reflection, while their powder is nearly black. When recrystallized from water, the compound gives the 2 : 1 salt, thus differing from the chloride. It was obtained from a solution containing 50 g. of cæsium bromide and 70 g. of copper bromide with sufficient water to form a volume of 200 c.c., and it continued to be produced as cupric bromide was added until the solution became saturated with that compound.

The following analyses were made of separate preparations which were obtained under wide variations of conditions.

	Found.				Calculated for $CsCuBr_3$.
Cs . . .	29.93	29.09	. . .	30.43	30.48
Cu . . .	14.72	15.09	14.73	14.81	14.53
Br . . .	55.09	54.96	. . .	64.96	54.99
	99.74	99.14		100.20	100.00

SHEFFIELD SCIENTIFIC SCHOOL,
September, 1893.

ON THE CÆSIUM-CUPROUS CHLORIDES.*

By H. L. WELLS.

The salts to be described were prepared by heating solutions containing cæsium chloride and cupric chloride with copper wire, and sufficient hydrochloric acid to prevent the formation of basic salts; then, after the copper in solution was chiefly in the form of cuprous chloride, cooling to crystallization.

When the solutions were dilute, cæsium chloride being in excess, very slender white prisms were obtained under wide variations of conditions. The crystals became yellowish while being dried with paper, but they were apparently nearly stable in the air when dry. It was found that the salt was decomposed by water. Two different products were analyzed.

	Found.		Calculated for $CsCl.Cu_2Cl_2$.
Cæsium	36.93	36.36	36.29
Copper	34.33	34.17	34.64
Chlorine	28.95	28.87	29.07

The results show that the formula $CsCu_2Cl_3$ belongs to this salt.

On using more concentrated solutions, also with an excess of cæsium chloride, thin, rectangular, colorless plates were produced, sometimes 10 or 20 mm. in diameter. The range of conditions under which this salt is produced is wide, and large crops of it are easily prepared. As the concentration of the cæsium chloride solutions was increased, the same compound appeared in the form of blade-like crystals with pointed ends. By dissolving this salt in water the previously described compound is produced by crystallization. The surface of the crystals becomes yellow on drying, but when dry it appears to

* Amer. Jour. Sci., xlvii, February, 1894.

be very stable. The first two analyses represent separate crops of the rectangular plates, the third a crop of the blade-like crystals.

	Found.			Calculated for $3CsCl.Cu_2Cl_2$.
	I.	II.	III.	
Cæsium	56.81	56.66	56.84	56.72
Copper	17.95	17.89	17.84	18.05
Chlorine	25.03	25.08	25.13	25.23

It is evident that this salt has the formula $Cs_3Cu_2Cl_5$.

With nearly or quite saturated cæsium chloride solutions containing comparatively little cuprous chloride, prismatic crystals are formed on cooling. The crystals are very pale yellow in color, and their lustre is less brilliant than that of the preceding compound. Crystals having a diameter of two or three millimeters and a length of several centimeters were sometimes observed. This salt forms under very narrow limits of conditions, and it is very difficult to obtain it free from the preceding salt, and especially from cæsium chloride, which usually crystallizes with it when the conditions are right for its formation. After a great many trials three crops which were satisfactory were obtained for analysis. The third analysis represents crystals which were picked out of the solution one at a time and separately pressed between smooth filter-papers. All the preparations were carefully examined under the microscope and were evidently pure.

	Found.			Calculated for $6CsCl.Cu_2Cl_2.2H_2O$.
Cæsium	64.77	65.07	64.09	64.10
Copper	9.38	9.42	10.04	10.20
Chlorine	22.70	22.83	. . .	22.81
Water (difference) .	3.15	2.69	3.14	2.89

The analyses show that the salt has the formula $Cs_3CuCl_4.H_2O$.

The previously described cuprous double halogen salts, with the new cæsium salts for comparison, are given below:

Cæsium Salts.	Previous Salts.
$CsCl.Cu_2Cl_2$	$4NH_4Cl.3Cu_2Cl_2$
$3CsCl.Cu_2Cl_2$	$2NH_4I.Cu_2I_2.H_2O$
$6CsCl.Cu_2Cl_2.2H_2O$	$4KCl.Cu_2Cl_2$
. . . . .	$4NH_4Cl.Cu_2Cl_2$

It is remarkable that there is no correspondence in type between the cæsium compounds and the others, and that such a variety of types appears to exist. The formula $4NH_4Cl.3Cu_2Cl_2$ may be considered somewhat doubtful on account of its complex ratio, and because with one-fourth less ammonium chloride it would correspond to the first cæsium salt.

The salt $Cs_3Cu_2Cl_5$ is noticeable on account of its rather complex formula and because it has the same ratio of cæsium to copper as the previously described cupric salt $Cs_3Cu_2Cl_7.2H_2O$. Since the latter has a ratio that is unique among the bivalent metal double halogen salts, a close structural relation between the two compounds is suggested.

These cæsium-cuprous chlorides show a decided lack of conformity with Remsen's law* concerning the composition of double halides. Two out of three of them fail to correspond to the law, while one of these, instead of not containing more than one CsCl for one CuCl, actually contains three times as much cæsium chloride as Remsen's law allows.

My thanks are due to Mr. L. C. Dupee, who prepared and analyzed one sample of the salt $CsCu_2Cl_3$.

SHEFFIELD SCIENTIFIC SCHOOL,
September, 1893.

* Amer. Chem. Jour., xi, 296; xiv, 85.

ON THE DOUBLE CHLORIDES AND BROMIDES OF CÆSIUM, RUBIDIUM, POTASSIUM, AND AMMONIUM WITH FERRIC IRON, WITH A DESCRIPTION OF TWO FERRO-FERRIC DOUBLE BROMIDES.

By P. T. WALDEN.

Previous investigation on the double ferric halides seems to have been devoted exclusively to the chlorides, and the metal cæsium has not as yet been worked with in this connection.

In view of these facts it appeared desirable to prepare, as far as possible, a complete series of the double halogen salts of the above-named metals. Only negative results were obtained, however, when attempts were made to prepare double iodides, so that the work was necessarily confined to the chlorides and bromides.

The following compounds have been previously described:

Rb_3FeCl_6	$K_2FeCl_5H_2O$
....	$(NH_4)_2FeCl_5H_2O$
....	$Na_2FeCl_5H_2O$

The existence of the above potassium and ammonium salts has been confirmed in the present investigation, but the compound Rb_3FeCl_6, described by Godeffroy,† could not be made, although a hydrous salt of the same type was prepared with cæsium. A most careful series of experiments using large quantities of the constituent chlorides was made in the attempt to prepare the rubidium salt just mentioned. It is not believed to be possible that Godeffroy obtained this compound, and his error was probably due to his neglecting the

* Amer. Jour. Sci., xlviii, October, 1894.

† Arch. Pharm. [3], ix, 343.

water of crystallization in the salt $Rb_2FeCl_5H_2$. There is not a great difference between the theoretical composition required by a 3 : 1 anhydrous compound and the 2 : 1 salt with one molecule of water, especially as far as the chlorine and iron are concerned. This can be seen from the following comparison:

	Calculated for Rb_3FeCl_6.	Calculated for $Rb_2FeCl_5H_2O$.
Rubidium . . .	48.83	40.44
Iron	10.65	13.29
Chlorine	40.52	42.01
Water	. . .	4.26
	100.00	100.00

Since the hydrous 2 : 1 salt is easily prepared, it therefore seems certain that this must have been the single salt described by Godeffroy.

The following is a list of the salts obtained:

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.
$Cs_3FeCl_6.H_2O$	$Cs_2FeCl_5.H_2O$	$CsFeCl_4.\frac{1}{2}H_2O$
. . . . .	$Cs_2FeBr_5.H_2O$	$CsFeBr_4$
. . . . .	$Rb_2FeCl_5.H_2O$	. . . . .
. . . . .	$Rb_2FeBr_5.H_2O$	. . . . .
. . . . .	$K_2FeCl_5.H_2O$*	. . . . .
. . . . .	. . . . .	. . . . .
. . . . .	$(NH_4)_2FeCl_5.H_2O$*	. . . . .
. . . . .	. . . . .	$NH_4FeBr_4.2H_2O$

It will be noticed that the type 2 : 1 is the most frequently recurring, being found in every case except with potassium and ammonium bromides. The salts of this type, as might be expected, are also the most stable and easily made, especially with cæsium chloride, where it is formed through a very wide range of conditions, leaving only a narrow margin for the other two members of the series. It is remarkable, in view of these facts, that this type should not have been obtained with

† These two salts have been previously described by Fritzsche, J. prakt. Chem., xviii, 483.

ammonium bromide, while the 1 : 1 type, which is comparatively unstable in other cases, is made without difficulty.

This investigation furnishes another striking example of the fact, already noticed several times in this laboratory, that cæsium halides form more complete series of double salts than the halides of the other alkali metals. With cæsium chloride we get a complete series, while with the chlorides of the other alkali metals only one type appears. In the bromides no double ferric potassium salt could be isolated, whereas two well-defined and comparatively stable compounds were obtained with cæsium.

Wells and Campbell * have called attention to the fact that, in a number of cases, double halides show an increase in ease of formation from the iodides to the chlorides. No better illustration could be had of this truth than the series of salts prepared in the present investigation, where the chlorides were made in greater number and with more ease than the bromides, while no iodides at all could be obtained.

Preparation. — All these salts were made by mixing solutions of the simple halides, evaporating and cooling to crystallization. It was found necessary in all cases to use solutions slightly acidified with the corresponding halogen acid, in order to prevent the formation of basic salts. A record, as nearly exact as possible, was kept of the relative quantities of the constituents used, and this has been indicated under each salt. The crystals were freed from the mother-liquor by pressing between smooth filter papers, and in every case where it was admissible they were further dried by exposure to the air of the laboratory. Where the salt was at all deliquescent it was at once removed to a tightly stoppered tube whose weight had been previously determined and weighed without loss of time. In this manner a quite unstable body could be analyzed and satisfactory results obtained. The purity of all the simple alkali halides was tested with the spectroscope before using. The very pure rubidium chloride used for this work was furnished to this laboratory for the encouragement of scientific

* Amer. Jour. Sci., III, xlvi, 432.

investigation by the firm of E. Merck of Darmstadt, through their agents, Messrs. Merck & Co. of New York, and our thanks are due to them for their unsolicited generosity.

Method of Analysis. — Iron was weighed as Fe_2O_3 in all cases, after having been separated from the alkali metal by precipitation with ammonia. The filtrate from this precipitation was evaporated to dryness, the alkali metal converted into sulphate and weighed as such after ignition in a stream of air containing ammonia. Ammonium was estimated by distilling with a solution of potassium hydroxide, absorbing the NH_3 liberated in hydrochloric acid and determining its amount by alkalimetry. Water was determined by combustion behind sodium carbonate and absorption in a washed calcium chloride tube. With $(NH_4)_2FeCl_5H_2O$ the water was removed by subjecting the salt to a temperature of 150° C. in an air bath for one hour.

The Double Chlorides. — These salts are all red except $CsFeCl_4\frac{1}{2}H_2O$, which is straw yellow. There is a distinct gradation in the shades of the salts of the type 2 : 1 from $(NH_4)_2FeCl_5H_2O$, which is a deep ruby red, growing lighter through the cæsium, rubidium, and potassium compounds until the last is very nearly the color of potassium dichromate.

3 : 1 Cæsium Ferric Chloride, $Cs_3FeCl_6H_2O$. — This salt is the only one of the 3 : 1 type which was prepared in the present investigation. It separated from a solution containing 50 g. of cæsium chloride and from .5 g. up to 2.5 g. of ferric chloride. The following analyses were made from separate crops:

	Found.			Calculated for $Cs_3FeCl_6H_2O$.
	A.	B.	C.	
Cæsium	58.30	58.42	. . .	58.17
Iron	7.91	7.85	. . .	8.17
Chlorine . . .	30.87	30.82	30.98	31.01
Water	2.74	2.72	2.64	2.65
	99.82	99.81		100.00

In color it closely resembles sodium dichromate. It is well crystallized in small prisms which are arranged in compact clusters radiating from a centre.

2 : 1 Cæsium, Rubidium, Potassium, and Ammonium Ferric Chlorides, $Cs_2FeCl_5H_2O$, $Rb_2FeCl_5H_2O$, $K_2FeCl_5H_2O$, and $(NH_4)_2FeCl_5H_2O$. — If solutions of the several alkali chlorides containing 50 g. each be made, it is necessary to add 3 g. of ferric chloride to make the cæsium salt of this type, 10 g. to make the rubidium salt, 15 g. to make the potassium salt, and 70 g. to make the ammonium salt. The cæsium, rubidium, and potassium compounds can be recrystallized unchanged, although with the last two there is a tendency to separate simple alkaline chlorides at the same time. Several separate crops were analyzed of each salt with the results shown below:

	Found.			Calculated for $Cs_2FeCl_5H_2O$.
	A.	B.	C.	
Cæsium	51.15	51.05	. . .	51.40
Iron	11.05	10.98	. . .	10.82
Chlorine . . .	34.36	34.19	34.02	34.30
Water	3.55	3.59	. . .	3.48
	100.11	99.81		100.00

	Found.		Calculated for $Rb_2FeCl_5H_2O$.
	A.	B.	
Rubidium . . .	40.51	40.69	40.44
Iron	13.28	13.33	13.29
Chlorine . . .	41.91	41.92	42.01
Water	4.23	4.20	4.26
	99.93	100.14	100.00

	Found.		Calculated for $K_2FeCl_5H_2O$.
	A.	B.	
Potassium . . .	23.66	23.54	23.73
Iron	16.86	16.99	16.98
Chlorine . . .	53.56	53.35	53.84
Water	6.20	5.96	5.45
	100.28	99.84	100.00

	Found.			Calculated for $(NH_4)_2FeCl_5H_2O$.
	A.	B.	C.	
Ammonium . .	12.39	12.36	12.00	12.52
Iron	19.13	18.95	. . .	19.48
Chlorine . . .	61.21	61.07	61.22	61.74
Water	7.39	. . .	. . .	6.26
	100.12			100.00

All these salts are well crystallized in short prisms. The cæsium and rubidium compounds are permanent in the air, but the potassium and ammonium salts absorb moisture quite rapidly.

1 : 1 Cæsium Ferric Chloride, $CsFeCl_4.\frac{1}{2}H_2O$. — This was made from a solution containing 50 g. of cæsium chloride and 180 g. of ferric chloride. Below are the analyses of separate crops:

	Found.			Calculated for $CsFeCl_4\frac{1}{2}H_2O$.
	A.	B.	C.	
Cæsium	38.39	38.53	. . .	39.39
Iron	17.03	16.85	. . .	16.48
Chlorine . . .	41.76	41.73	41.98	41.77
Water	3.14	3.63	4.03	2.36
	100.32	100.74		100.00

This salt absorbs moisture in the air so rapidly that considerable difficulty was experienced in preparing samples for analysis. It is regarded as containing half a molecule of water on the evidence of the analytical results, although it is not unreasonable to suppose that all the water found was absorbed, especially as the bromide, $CsFeBr_4$, is anhydrous. The crystals were slender needles, which rapidly lost their yellow color in the air, turning red.

The Double Bromides. — These are all very dark green, almost black and quite opaque. Like the chlorides, the 2: 1 cæsium salt is darker than the rubidium compound of the same type. As no corresponding potassium or ammonium salt could be made, the comparison can be carried no farther. The cæsium and ammonium 1: 1 bromides are of nearly the same color. None of the double bromides are capable of recrystallization.

2 : 1 Cæsium and Rubidium Ferric Bromides, $Cs_2FeBr_5H_2O$ *and* $Rb_2FeBr_5H_2O$. — The first of these salts was made with the quantities of the constituent bromides about equal, the second with 50 g. of rubidium bromide to 60 g. of ferric bromide. The following are the analyses:

	Found. A.	Found. B.	Calculated for $Cs_2FeBr_5H_2O$.
Cæsium	35.76	35.60	35.95
Iron	8.05	7.93	7.56
Bromine	54.20	54.15	54.05
Water	2.52	2.84	2.44
	100.53	100.52	100.00

	Found. A.	Found. B.	Calculated for $Rb_2FeBr_5H_2O$.
Rubidium	26.20	26.14	26.51
Iron	8.86	8.99	8.68
Bromine	62.13	62.12	62.02
Water	2.90	2.88	2.79
	100.09	100.13	100.00

Both compounds were obtained in short doubly terminated prisms. The cæsium salt is comparatively stable, while the rubidium salt decomposes rapidly in the air.

1 : 1 Cæsium and Ammonium Ferric Bromides, $CsFeBr_4$ and $NH_4FeBr_4 2H_2O$. — A solution of 50 g. of cæsium bromide and 100 g. of ferric bromide gave the first of these salts in slender needles. The second could not be obtained until 250 g. of ferric bromide had been added to 50 g. of ammonium bromide. Separate crops of each were analyzed with the results given below.

	Found. A.	Found. B.	Calculated for $CsFeBr_4$.
Cæsium	26.02	. . .	26.13
Iron	11.25	11.30	11.00
Bromine	63.01	62.99	62.87
	100.28		100.00

	Found. A.	Found. B.	Found. C.	Calculated for $NH_4FeBr_4 2H_2O$.
Ammonium . . .	3.98	3.92	3.83	4.19
Iron	13.48	13.59	. . .	13.02
Bromine	74.85	74.71	. . .	74.42
Water	7.69*	7.78*	. . .	8.37
	100.00	100.00		100.00

* Water by difference.

As the ammonium salt is so deliquescent that no satisfactory determination of water was possible, it was taken by difference, and it is believed that the results warrant the acceptance of the formula as written above. Great care was exercised in an attempt to prepare a 2 : 1 ammonium bromide, but without success. $NH_4FeBr_42H_2O$ and simple ammonium bromide were finally crystallized out together in the same solution. This is regarded as good evidence that no salt of a type higher in ammonium exists.

Ferro-ferric Salts: $RbBr.FeBr_2.2FeBr_3.3H_2O$ and $KBr.FeBr_2.2FeBr_3.3H_2O$. — While endeavoring to obtain a double ferric bromide with potassium, a dark green body separated from a solution containing an excess of bromine, which gave a black hydroxide with ammonia. This was considered so remarkable that an effort was made to prepare corresponding salts with the other alkali halides and ammonium, under the same conditions. This attempt resulted in the formation of only one other compound of the same kind, that with rubidium. The ferrous iron in those salts was determined by titration in the presence of hydrochloric acid with a standard potassium dichromate solution. It was found to be impossible to determine water satisfactorily on account of the extreme instability of both salts. It was therefore taken by difference. The rubidium salt resulted from the bringing together in solution of 50 g. of rubidium bromide and 150 g. of ferric bromide, the potassium salt from a solution of 50 g. of potassium bromide and 250 g. of ferric bromide. Below are the analytical results, A, B, and C being separate crops.

	Found.			Calculated for $RbBr.FeBr_2.2FeBr.3H_2O$.
	A.	B.	C.	
Rubidium . . .	7.25	. . .	. . .	8.32
Ferrous iron . .	5.17	5.16	5.53	5.45
Ferric iron . .	11.10	10.71	10.13	10.90
Bromine . . .	68.83	68.37	68.48	70.07
Water . . .	7.65*	. . .	. . .	5.26
	100.00			100.00

* Water by difference.

	Found.		Calculated for $KBr.FeBr_2.2FeBr_3.3H_2O$.
Potassium	3.47	3.92	3.98
Ferrous iron	4.31	4.26	5.71
Ferric iron	12.36	11.70	11.42
Bromine	73.15	73.09	73.39
Water	6.71*	. . .	5.50
	100.00		100.00

These salts are dark green in color and quite opaque, like the double ferric bromides described above. The crystallization of the rubidium salt is apparently rhombohedral, that of the potassium cubical.

In conclusion the author wishes to express his sincere thanks to Prof. H. L. Wells, under whose direction the work has been carried on, for his kindly aid and many valuable suggestions.

SHEFFIELD SCIENTIFIC SCHOOL,
July, 1894.

* Water by difference.

ON THE CÆSIUM-COBALT AND CÆSIUM-NICKEL DOUBLE CHLORIDES, BROMIDES, AND IODIDES.

By G. F. CAMPBELL.

As a continuation of the work in this laboratory on double halogen salts, the investigation of the above-mentioned compounds has been taken up. The study has been made in a systematic manner with the view of preparing as complete a series as possible. The salts obtained belong to three types, and are as follows:

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.
Cs_3CoCl_5	Cs_2CoCl_4	$CsCoCl_3.2H_2O$
Cs_3CoBr_5	Cs_2CoBr_4	. . . . .
. . . .	Cs_2CoI_4	. . . . .
. . . .	. . . .	$CsNiCl_3$
. . . .	. . . .	$CsNiBr_3$

The results show that cobalt forms double salts with much greater facility than nickel, for with the latter metal only the chloride and bromide of a single type could be obtained.

The series illustrates the increase in ease of formation of double salts from the iodides to the chlorides, which has been previously observed, especially in the case of the cæsium-magnesium salts by Wells and Campbell.* No cæsium-nickel iodide could be prepared.

It should be noticed that the two salts of the 3 : 1 type are exceptions to Remsen's law concerning this class of bodies.

The previously described double halogen salts of cobalt and nickel, as far as I have been able to learn, correspond to two types of the cæsium salts, and are as follows:

* Amer. Jour. Sci., xlviii, November, 1894. † Ibid., xlvi, 432.

2 : 1 Type.	1 : 1 Type.
$(NH_4)_2CoF_4.2H_2O$	$NH_4CoCl_3.6H_2O$
$(NH_4)_2NiF_4.2H_2O$	$NH_4NiCl_3.6H_2O$
. . . . .	$KCoF_3.H_2O$
. . . . .	$KNiF_3.H_2O$
. . . . .	$NaCoF_3.H_2O$
. . . . .	$NaNiF_3.H_2O$

The following table gives approximately the composition of the solutions from which the cæsium salts under consideration were crystallized by concentration and cooling:

	Cs : Co or Ni (Atoms.)	
Cs_3CoCl_5 . . .	From 12 : 1 to 6 : 1	
Cs_2CoCl_4 . .	" 6 : 1 " 0.4 : 1	
$CsCoCl_3.2H_2O$ . .	" 0.4 : 1 "	syrupy solution of $CoCl_2$
Cs_3CoBr_5 . . .	" 2 : 1 " 1 : 1	
Cs_2CoBr_4 . . .	" 1 : 1 "	syrupy solution of $CoBr_2$
Cs_2CoI_4	" 1 : 4 " 1 : 16	
$CsNiCl_3$ . . .	" 12 : 1 "	syrupy solution of $NiCl_2$
$CsNiBr_3$	" 2.5 : 1 "	syrupy solution of $NiBr_2$

More or less of the corresponding halogen acid was present in each case, and an increase of this was apparently equivalent in effect to the addition of the cæsium halide. In the case of the two nickel salts, a rather large amount of the acid was desirable, for if it was not present, the salts appeared only upon heating the concentrated solutions and dissolved when they cooled.

The color of the chlorides containing cobalt is a magnificent blue, the bromides and the iodides containing the same metal are green, while the two nickel salts are yellow. The two nickel salts form almost microscopic crystals. The two salts of the 3 : 1 type were obtained in crystals having a diameter of about 5 mm., apparently combinations of the cube and octahedron. The salts of the 2 : 1 type form large plates or prisms, the habit evidently depending upon the composition of the solutions from which they crystallize. The salt $CsCoCl_3.2H_2O$ forms rather small plates. Besides the blue salt just men-

tioned, a red cæsium-cobalt chloride of the 1 : 1 type was obtained which lost water of crystallization so readily, with change of color, that it could not be analyzed in its original condition.

The compound Cs_2CoI_4 is deliquescent, while the other salts, here described, are stable. All the salts are whitened when brought into contact with water or alcohol, evidently on account of decomposition.

The following analyses were made:

Cs_3CoCl_5.

	Cæsium.	Cobalt.	Chlorine.
Found	62.79	9.16	27.83
Calculated	62.82	9.24	27.74

Cs_2CoCl_4.

	Cæsium.	Cobalt.	Chlorine.
Found	56.86	12.53	30.40
Calculated	56.99	12.58	30.43

$CsCoCl_3.2H_2O$.

	Cæsium.	Cobalt.	Chlorine.	Water.
Found	38.64	17.67	32.07	10.94
Calculated	39.80	17.56	31.87	10.77

Cs_3CoBr_5.

	Cæsium.	Cobalt.	Bromine.
Found A	46.65	6.88	46.33
" B	...	7.44	46.97
" C	45.81	7.08	46.52
Calculated	46.52	6.84	46.64

Cs_2CoBr_4.

	Cæsium.	Cobalt.	Bromine.
Found A	41.21	9.49	49.43
" B	...	9.20	49.60
" C	...	9.25	49.32
Calculated	41.26	9.10	49.64

Cs_2CoI_4.

	Cæsium.	Cobalt.	Iodine.
Found A	29.69	7.10	. . .
" B	. . .	7.34	60.24
" C	. . .	7.31	60.29
Calculated	31.93	7.09	60.98

$CsNiCl_3$.

	Cæsium.	Nickel.	Chlorine.
Found A	44.42	19.70	35.78
" B	. . .	19.14	35.57
Calculated	44.61	19.66	35.73

$CsNiBr_3$.

	Cæsium.	Nickel.	Bromine.
Found A	29.93	13.83	55.84
" B	30.60	13.58	55.49
Calculated	30.81	13.58	55.61

The author takes pleasure in expressing his indebtedness to Prof. H. L. Wells for valuable advice in connection with this investigation.

SHEFFIELD SCIENTIFIC SCHOOL,
September, 1894.

ON THE DOUBLE HALIDES OF CÆSIUM, RUBIDIUM, SODIUM, AND LITHIUM WITH THALLIUM.*

By J. H. PRATT.

In previous investigations upon the double halides of trivalent thallium with the alkali metals, the salts of only potassium and ammonium seem to have been carefully studied. The only cæsium and rubidium salts that have been made are $Cs_3TlCl.2H_2O$ and $Rb_3TlCl_6.2H_2O$ described by Godfrey,* but in the present investigation the compounds of this type were found to have one instead of two molecules of water of crystallization.

The present research has been carried out very carefully and systematically in order to obtain as complete a series of double salts in each case as possible. The salts that have been made belong to four types, corresponding to those previously made with potassium and ammonium, and are as follows:

3 : 1	2 : 1	3 : 2	1 : 1
$Cs_3TlCl_6.H_2O$	Cs_2TlCl_5	$Cs_3Tl_2Cl_9$	. . . . .
. . . . .	$Cs_2TlCl_5.H_2O$	. . . . .	. . . . .
. . . . .	. . . . .	$Cs_3Tl_2Br_9$	$CsTlBr_4$
. . . . .	. . . . .	. . . . .	$CsTlI_4$
$Rb_3TlCl_6.H_2O$	$Rb_2TlCl_5.H_2O$	. . . . .	. . . . .
$Rb_3TlBr_6.H_2O$	. . . . .	. . . . .	$RbTlBr_4.H_2O$
. . . . .	. . . . .	. . . . .	$RbTlI_4.2H_2O$
$Na_3TlCl_6.12H_2O$	. . . . .	. . . . .	. . . . .
$Li_3TlCl_6.8H_2O$	. . . . .	. . . . .	. . . . .

For comparison, a list of the previously described double salts with potassium and ammonium is also given.

* Amer. Jour. Sci., xlix, May, 1895. † Landenberg's Handwörterbuch.

3 : 1	2 : 1	3 : 2	1 : 1
$K_3TlCl_6.2H_2O$	$K_2TlCl_5.3H_2O$	$K_3Tl_2Cl_9.1\frac{1}{2}H_2O$	$KTlBr_4$
$(NH_4)_3TlCl_6.2H_2O$	. . . . .	$K_3Tl_2Br_9.1\frac{1}{2}H_2O$	$KTlI_4.H_2O$
$(NH_4)_3TlCl_6$	. . . . .	. . . . .	$(NH_4)TlBr_4.5H_2O$
. . . . .	. . . . .	. . . . .	$(NH_4)TlBr_4.2H_2O$
. . . . .	. . . . .	. . . . .	$(NH_4)TlBr_4$
. . . . .	. . . . .	. . . . .	$(NH_4)TlI_4$

Several points of interest, already noticed in connection with double salts prepared in this laboratory, are well illustrated by the series of new compounds to be described. With cæsium, a more complete series of salts was prepared than with the other alkali metals; and there is also an increase in ease of formation and in number of salts, from the iodides to the chlorides. The salts, formed from the alkali metal with the lower atomic weight are generally more soluble in water, form in larger crystals and with more water of crystallization than those with higher atomic weight.

Preparation. — The double salts were prepared in each case by mixing solutions of the thallic halide with the alkali halide in widely varying proportions, evaporating and cooling to crystallization. With the bromides and iodides the conditions for obtaining the double salts were improved by the presence of a little free bromine and iodine.

The crystals, soon after forming, were removed from the solutions, quickly pressed between filter papers to remove the mother-liquor, and, with the exception of the sodium and lithium salts, allowed to stand exposed to the air for some time. The latter, on account of their instability, were placed in tightly stoppered weighing-tubes as soon as they were free from the mother-liquor.

Method of Analysis. — In determining thallium, the salt was dissolved in warm water and a slight excess of ammonium sulphide added to precipitate the thallium as thallous sulphide. This was filtered and washed with water containing a little ammonium sulphide. The precipitate was then dissolved in hot dilute nitric acid, the solution evaporated with sulphuric acid in a platinum crucible, and then heated to constant weight

within a porcelain crucible over a small flame. The filtrate from the thallous sulphide precipitation was evaporated with sulphuric acid, the ammonium salts driven off, and the residual alkali sulphate ignited in a stream of air containing ammonia. The halogens were determined as silver salts in separate portions, with the precaution of adding sulphurous acid in the case of the iodides to prevent loss of iodine in dissolving, and it was found to be necessary in all cases to use a large excess of nitric acid in order to obtain the silver halide in a pure condition. Water was determined by igniting in a combustion tube, behind a layer of dry sodium carbonate, in a stream of dry air and collecting it in a weighed calcium chloride tube.

3 : 1 Cæsium and Rubidium Thallic Chlorides, $Cs_3TlCl_6.H_2O$ and $Rb_3TlCl_6.H_2O$. — The cæsium salt is obtained, as a white precipitate, when 0.25 g. of thallic chloride is added to a solution of 50 g. of cæsium chloride. The precipitate dissolves somewhat slowly upon heating the solution, and crystallizes out on cooling. The range of conditions is very narrow as 3 g. of thallic chloride to 50 g. of cæsium chloride give the salt, Cs_3TlCl_9. The salt is soluble in hot water, but $Cs_3Tl_2Cl_9$ crystallizes from the solution.

The rubidium salt has a much wider range of formation. It is obtained when 1.5 to 25 g. of thallic chloride are added to a solution of 40 g. of rubidium chloride. It is very soluble in cold water, but gives another salt, $Rb_2TlCl_5.H_2O$ upon crystallization. Both salts are white, as are all the chlorides with one exception. Two separate crops of each were analyzed with the following results:

	Found.			Calculated for $Cs_3TlCl_6.H_2O$.
	A.	B.		
		I.	II.	
Cæsium . . .	48.44	48.05	48.33	47.84
Thallium . . .	24.21	24.45	24.37	24.46
Chlorine . . .	25.37	25.53	. . .	25.54
Water	2.74	1.97	. . .	2.16

	Found.		Calculated for $Rb_3TlCl_6.H_2O$.
	A.	B.	
Rubidium . . .	. . .	36.54	37.09
Thallium . . .	29.02	29.65	29.50
Chlorine	30.99	31.17	30.81
Water	2.51	1.72	2.60

The cæsium salt was obtained in hair-like crystals, too small for measurement. The rubidium salt crystallized in thin plates having a rhombic outline. Under the microscope these showed an extinction parallel to the diagonals and in convergent light a bisectrix at one side of the field, with the plane of the optic axes at right angles to the longer diagonal, indicating monoclinic symmetry.

2 : 1 Cæsium and Rubidium Thallic Chlorides, Cs_2TlCl_5, $Cs_2TlCl_5.H_2O$, and $Rb_2TlCl_5.H_2O$. — The anhydrous cæsium salt is formed when 5 to 8 g. of thallic chloride are added to a somewhat concentrated solution of 100 g. of cæsium chloride, and the hydrous salt, when 8 to 15 g. of thallic chloride are added to a more dilute solution of 100 g. of cæsium chloride. The rubidium salt was observed when 1.25 to 18 g. of rubidium chloride were added to a rather concentrated solution of 30 g. of thallic chloride. The two hydrous salts are white and the anhydrous compound is pale green. The cæsium salts are readily soluble in hot water, but the salt $Cs_3Tl_2Cl_9$ crystallizes from the solution. The rubidium salt recrystallizes unchanged from water. The following analyses were made upon separate crops:

	Found.			Calculated for Cs_2TlCl_5.
	A.	B.		
		I.	II.	
Cæsium . . .	. . .	40.46	40.17	41.07
Thallium . . .	31.11	31.82	31.62	31.52
Chlorine . . .	27.19	27.30	27.20	27.41
Water	.81	. . .	.81	. . .

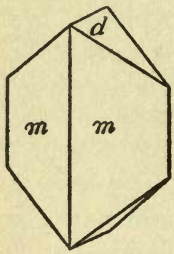
The small amount of water found in the above analyses, equivalent to about one-fourth of a molecule, was probably held mechanically by the crystals.

	Found.				Calculated for $Cs_2TlCl_5.H_2O$.
	A.		B.	C.	
	I.	II.			
Cæsium . .	40.03	39.84	40.30	39.85	39.97
Thallium . .	30.75	30.71	31.11	30.98	30.65
Chlorine . .	26.85	. . .	26.56	26.93	26.67
Water	. . .	. . .	2.88	2.37	2.71

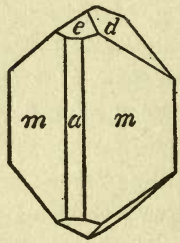
	Found. A.	Found. B.	Calculated for $Rb_2TlCl_5.H_2O$.
Rubidium . . .	29.09	28.97	29.97
Thallium . . .	35.94	35.74	35.76
Chlorine . . .	30.74	30.97	31.11
Water	3.34	. . .	3.16

The crystals of Cs_2TlCl_5 were in needles too small for measurement.

1.



2.



The crystallization of $Cs_2TlCl_5.H_2O$ and $Rb_2TlCl_5.H_2O$ is orthorhombic. The salts are similar in habit and are developed as in Figs. 1 and 2. The forms observed are as follows:

a, 100	*d*, 011
m, 110	*e*, 102

The crystals of the cæsium salt were only about .4 to .6 mm. in length, but the faces were smooth and gave good reflections on the goniometer. The axial ratio is,

$$\breve{a} : \bar{b} : \dot{c} = 0.6762 : 1 : 0.6954.$$

	Measured.	Calculated.
$d \wedge d$, 011 ∧ 0$\bar{1}$1	*70°	. . .
$m \wedge m$, 110 ∧ 1$\bar{1}$0	*68° 22′	. . .
$m \wedge a$, 110 ∧ 100	34° 3′ 30″	34° 11′
$a \wedge e$, 100 ∧ 102	62° 51′	62° 44′
$m \wedge d$, 110 ∧ 011	71° 14′; 71° 16′	71° 12′
$d \wedge e$, 011 ∧ 102	43° 9′	43° 16′
$e \wedge e$, 102 ∧ $\bar{1}$02	54° 6′	54° 32′

Crystals of the rubidium salt were obtained from about 1.5 to 4 mm. in length. The axial ratio is,

$$\breve{a} : \bar{b} : \dot{c} = 0.6792 : 1 : 0.7002.$$

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	Measured.	Calculated.
$d \wedge d$, 011 ∧ 0$\bar{1}$1	*69° 36′	. . .
$m \wedge m$, 110 ∧ 1$\bar{1}$0	*68° 7½′	. . .
$m \wedge a$, 110 ∧ 100	34° 4′; 34° 9′; 34° 5′	34° 4′
$a \wedge e$, 100 ∧ 102	62° 52½′	62° 49′
$m \wedge d$, 110 ∧ 011	71° 26′; 71° 23′	71° 21′
$d \wedge e$, 011 ∧ 102	43° 19′	43° 4½′
$e \wedge e$, 102 ∧ $\bar{1}$02	54° 15′	54° 22′

3 : 2 Cæsium Thallic Chloride, $Cs_3Tl_2Cl_9$. — The conditions under which this salt can be made are very wide; .5 to 29 g. of cæsium chloride form a heavy white precipitate when added to a solution of 40 g. of thallic chloride. This dissolves readily in the solution upon heating and crystallizes in slender hexagonal prisms terminated by the pyramid. When the ratio of the cæsium chloride to the thallic chloride is 30 g. to 50 g., a salt is obtained which crystallizes in hexagonal plates. Analyses of the plates do not agree very closely with theory, but it is evident that they are the same as the prismatic salt with another crystalline habit. The high percentage of cæsium and the corresponding low percentage of thallium is probably due to the slight inclusions held by the crystals, which could be seen with the microscope. This salt is white, permanent in the air, and recrystallizes unchanged from water. The analyses given below are of separate crops made under very different conditions.

	Cæsium.	Thallium.	Chlorine.	Water.
A	34.93	. . .	. . .	.65
B	35.09	35.64–35.51	28.09–27.99	. .
C	. . .	. . .	28.06	.95
D	. . .	35.63	. . .	. .
E	35.03	35.69	28.06	. .
F (Plates) .	36.64	33.85	28.15	. .
G (Plates) .	36.18	34.46	28.18	.61
Calculated for $Cs_3Tl_2Cl_9$.	35.42	36.22	28.36	. .

The water found in these analyses was probably held mechanically by the crystals.

The prismatic variety of this salt showed only the forms of the prism, $10\bar{1}0$, and pyramid, $10\bar{1}1$.

Axis $c = 0.82566$; $0001 \wedge 10\bar{1}1 = 43° 37' 50''$

	Measured.	Calculated.
$p \wedge p$, $10\bar{1}1 \wedge 01\bar{1}1$	*40° 21′ . . .	. . .
$m \wedge p$, $10\bar{1}0 \wedge 10\bar{1}1$	46° 21½′; 46° 22′	46° 22′

Sections parallel to the basal plane show in convergent polarized light the normal uniaxial interference figure, with weak negative double refraction. The crystals served very well as 60° prisms for the determination of the indices of refraction with the following results:

	Red, Li.	Yellow, Na.	Green, Tl.
$\omega =$	1.772	1.784	1.792
$\epsilon =$	1.762	1.774	1.786

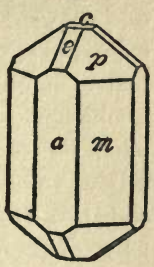
3 : 1 Rubidium Thallic Bromide, $Rb_3TlBr_6.H_2O$. — This salt was formed, when 1.5 to 24 g. of thallic bromide were added to a very concentrated solution of 50 g. of rubidium bromide. It crystallizes in beautiful golden yellow crystals, which are very soluble in water, giving the 1 : 1 salt on recrystallizing. Careful efforts were made to obtain a 2 : 1 and 3 : 2 rubidium thallic bromide, but without success. Several separate products, made under very different conditions, were analyzed with the results which follow:

	Rubidium.	Thallium.	Bromine.	Water.
A	28.57	. . .	49.29	2.49
B	. . .	20.39	49.66	. . .
C	28.18	20.59	. . .	. . .
D	28.03	20.16	49.42	. . .
E	27.70	20.33	50.28	. . .
F	. . .	20.64	. . .	. . .
G	26.56	21.17	50.49	. . .
Calculated for $Rb_3TlBr_6.H_2O$	26.76	21.28	50.08	1.88

The somewhat high percentage of rubidium and the low percentage of thallium found in the first four analyses is prob-

ably due to the large excess of rubidium bromide in the concentrated solutions from which the crystals were obtained. As more thallic bromide was added, better crystals were obtained in more dilute solutions, which give percentages agreeing very well with the calculated.

3.



The crystallization of this salt is tetragonal. Doubly terminated crystals were obtained up to a length of 6 mm.

The forms observed are:

a, 100	*m*, 110	*p*, 111
c, 001	*e*, 101	

The habit is shown in Fig. 3.

Axis $\dot{c} = 0.80728$; $001 \wedge 101 = 38° 54' 45''$

	Measured.	Calculated.
$e \wedge e$, $101 \wedge 101$	*77° 49½′	. . .
$a \wedge e$, $100 \wedge 101$	51° 6′; 51° 2′; 51° 3½′	51° 5½′
$a \wedge p$, $100 \wedge 111$	57° 52′; 57° 54′; 57° 53′	57° 52′
$e \wedge p$, $101 \wedge 111$	32° 5′; 32° 12′	32° 8′
$c \wedge p$, $001 \wedge 111$	48° 51′; 48° 55′	48° 46′
$m \wedge p$, $110 \wedge 111$	41° 7′; 41° 4′	41° 13′

The crystals show a weak negative double refraction.

3 : 2 Cæsium Thallic Bromide, $Cs_3Tl_2Br_9$. — This salt was observed, as yellowish red crystals, when 1 to 15 g. of thallic bromide were added to a solution of 50 g. of cæsium bromide. It was always obtained in small striated crystals, which were not adapted for measurement. It is permanent in the air and recrystallizes unchanged from water. Analyses of separate products gave the following results:

	Found.				Calculated for $Cs_3Tl_2Br_9$.
	A.	B.	C.	D.	
Cæsium . . .	. . .	26.52	26.14	. . .	26.13
Thallium . .	27.36	27.21	27.28	. . .	26.72
Bromine . .	47.24	47.14	47.08	47.27	47.15

1 : 1 Cæsium and Rubidium Thallic Bromides, $CsTlBr_4$ and $RbTlBr_4.H_2O$. — These two salts are of nearly the same color, pale yellow. The rubidium compound, which retains its lustre and color much better than the other, recrystallizes unchanged from water, while the cæsium salt gives $Cs_3Tl_2Br_9$, when its solution is evaporated to crystallization. The cæsium salt was observed when 2 to 10 g. of cæsium bromide were added to 40 g. thallic bromide, and the rubidium salt when 3 to 24 g. of rubidium bromide were added to 40 g. thallic bromide. Analyses of several different crops gave the following results:

	Found.				Calculated for $CsTlBr_4$.
	A.	B.	C.	D.	
Cæsium . . .	19.14	. . .	. . .	20.44	20.25
Thallium . .	32.36	31.79	32.04	. . .	31.05
Bromine	47.76	. . .	48.39	48.88	48.70

	Found.			Calculated for $RbTlBr_4.H_2O$.
	A.	B.	C.	
Rubidium . . .	13.77	13.41	13.91	13.63
Thallium	32.18	. . .	. . .	32.51
Bromine	50.06	. . .	50.30	50.99
Water	3.80	. . .	. . .	2.87

The crystallization of these two salts is isometric, the cube being the only form observed.

1 : 1 Cæsium and Rubidium Thallic Iodides, $CsTlI_4$ and $RbTlI_4.H_2O$. — Both of these salts were prepared from solutions containing a large excess of thallic iodide and also from solutions containing a large excess of the alkali iodide, so that no other type of double iodides with these two metals could be obtained. As the thallic iodide was very difficultly soluble in water, alcoholic solutions were used where the thallic iodide was in excess. The salts are ruby red, with a brilliant lustre, which is slowly lost in the air. Both are decomposed by water. The analytical results obtained from several different crops are given below:

	Found.			Calculated for $CsTlI_4$.
	A.	B.	C.	
Cæsium	16.57	16.38	. . .	15.74
Thallium	24.09	24.04	. . .	24.14
Iodine	. . .	59.48	59.67	60.12

	Found. A.	Found. B.	Calculated for $RbTlI_4.2H_2O$.
Rubidium . .	10.34	9.78	10.26
Thallium . . .	24.98	25.23	24.47
Iodine	60.38–60.32	60.79	60.94
Water	4.50	. . .	4.32

These salts crystallize in the isometric system, the habit being usually the cube truncated by the octahedron.

3 : 1 Sodium and Lithium Thallic Chlorides, $Na_3TlCl_6.12H_2O$ and $Li_3TlCl_6.8H_2O$. — Only one type of double salts could be obtained with these metals, and it does not seem possible that others exist, for the ground was covered very carefully and systematically. On account of the extreme solubility of these salts, especially that of the lithium compound, the solutions had to be kept very concentrated, in a more or less syrupy condition, which accounts for the high alkali metal and low thallium found. These salts are transparent and colorless when first taken from the mother-liquor, but, upon exposure to the air, the sodium salt becomes opaque and the lithium compound deliquesces. Analyses of different products gave the following results:

	Found. A.	Found. B.	Calculated for $Na_3TlCl_6.12H_2O$.
Sodium	11.13	10.48	9.83
Thallium	27.79	28.39	29.06
Chlorine	31.23	30.45	30.34
Water	. . .	29.75	30.77

	Found. A.	B.	C.	D.	Calculated for $Li_3TlCl_6.8H_2O$.
Lithium . .	3.71	3.79	3.73	3.78	3.61
Thallium .	34.51	. . .	. . .	. . .	35.06
Chlorine. .	36.09	36.01	36.40	36.31	36.59
Water . .	25.14*	. . .	. . .	. . .	24.74

On account of the instability of the sodium and lithium salts no crystallographic determinations were made.

Repeated attempts to prepare lithium and sodium thallic

* By difference.

bromides were entirely without success, hence no attempt was made to prepare the iodides.

The author wishes to express his indebtedness to Prof. H. L. Wells for valuable advice in connection with the chemical part of this work, and to Prof. S. L. Penfield for suggestions concerning the crystallography.

SHEFFIELD SCIENTIFIC SCHOOL,
December, 1894.

ON THE DOUBLE SALTS OF CÆSIUM CHLORIDE WITH CHROMIUM TRICHLORIDE AND WITH URANYL CHLORIDE.*

By H. L. WELLS and B. B. BOLTWOOD.

Neumann† has made an extensive investigation of the double salts formed with chromium trichloride and the chlorides of several other metals, not, however, including cæsium. He obtained a violet double salt in each case with ammonium, potassium, rubidium, beryllium, and magnesium, corresponding to the general formula, $2M'Cl.CrCl_3.H_2O$, while with lithium, sodium, calcium, strontium, barium, zinc, and cadmium he was unable to prepare any double compounds. The double fluorides, $2NH_4F.CrF_3.H_2O$, and $2KF.CrF_3.H_2O$, which are analogous to Neumann's salts, have been mentioned by Wagner,‡ who also prepared the compounds $4NaF.2CrF_3.H_2O$ and $3NH_4F.CrF_3$. The existence of the latter salt has been confirmed by Petersen.§

Since Neumann had not prepared any cæsium-chromium chloride, and because, from the well-known comparative insolubility of cæsium double salts, it seemed possible that a greater variety of compounds would be obtained with this than with other metals, we have undertaken an investigation in this direction. As the result of a systematic search, however, we have added only a variation in water of crystallization to Neumann's general formula.

Two salts have been obtained. One of these, $2CsCl.CrCl_3.H_2O$, is violet in color, corresponding exactly to Neumann's compounds, while the other, $2CsCl.CrCl_3.4H_2O$, is green. The violet salt was prepared by saturating warm aqueous solutions containing various proportions of the two simple chlorides with gaseous hydrochloric acid. The green salt was

* Amer. Jour. Sci., l, 1895.

† Liebig's Annalen, ccxliv, 329.

‡ Berichte, xix, 896.

§ J. prakt. Chem., II, lx, 52.

obtained from cold solutions by the use of hydrochloric acid, and without its use by evaporation over sulphuric acid.

The salt $2CsCl.CrCl_3.H_2O$ forms aggregates of very minute crystals of a magnificent red-violet color. It is stable in the air and does not lose its water at 160°. It is very slowly soluble in cold water, forming a green solution from which the green salt is deposited upon evaporation at ordinary temperatures. The four crops analyzed were prepared with amounts of cæsium chloride and chromic chloride varying from 15 g. of the first and 50 g. of the second to 50 g. of the first and 10 g. of the second. Gaseous hydrochloric acid caused a deposition of the salt from warm solutions. The products, after careful drying with paper and over sulphuric acid, gave the following results upon analysis:

	Found.				Calculated for $2CsCl.CrCl_3.H_2O$.
	A.	B.	C.	D.	
Cæsium . .	50.31	49.72	49.64	. . .	51.79
Chromium .	10.44	10.53	10.68	10.70	10.15
Chlorine . .	34.65	34.77	34.37	. . .	34.56
Water . . .	4.11	5.12	. . .	. . .	3.50
	99.51	100.14			100.00

The salt $2CsCl.CrCl_3.4H_2O$ is deposited from cold concentrated solutions in the form of green, apparently monoclinic crystals. It is somewhat deliquescent, very soluble in water, and loses no water in the desiccator over sulphuric acid. At 110° it readily loses three molecules of water and is converted into the violet salt. Three crops analyzed were prepared as follows: Crop A, by evaporating a solution of 50 g. cæsium chloride and 25 g. of chromic chloride; Crop B, by dissolving the violet salt in water and evaporating over sulphuric acid; Crop C, by cooling a concentrated solution of 50 g. of each chloride with the aid of ice and saturating it with hydrochloric acid. The results were as follows:

	Found.			Calculated for $2CsCl.CrCl_3.4H_2O$.
	A.	B.	C.	
Cæsium	46.40	46.13	46.73	46.86
Chromium . . .	9.80	9.53	10.79	9.19
Chlorine	31.30	31.14	. . .	31.27
Water	. . .	. . .	. . .	12.68

A determination was also made of the water lost at 110° :

	Found.	Calculated for $3H_2O$ in $2CsCl.CrCl_3.4H_2O$.
Water	9.90	9.51

The variation in color of the two salts that have just been described is interesting in connection with the violet and green modifications of chromic salts in general, which have furnished the ground for much investigation and discussion. In the case under consideration the transformation from one color to the other is accomplished by the addition or subtraction of water. It seems highly probable, however, that the change in water is accompanied by a fundamental change in the molecular structure, because the violet salt, containing the smaller amount of water, is very much more slowly soluble in water than the green salt, forming like the latter a green solution. We have found that the whole of the chlorine in the cold green solutions of these cæsium salts is not precipitated as silver chloride, thus showing that they agree in this respect with other green solutions of chromic chloride.

It is a curious circumstance that the green chromic sulphate has been considered * to contain less water than the violet modification, while with our cæsium salts exactly the reverse is true, the green salt containing the larger amount of water. It is also remarkable that, while violet chromic solutions are turned green by heat, our violet salt, nevertheless, is produced in hot solutions and the green salt in cold ones. The theory advanced by Krüger and maintained by Van Cleeff † that the green color of chromic sulphate solutions is due to the formation of a basic salt and free acid or an acid salt, seems hardly applicable to the green cæsium salts, since it crystallizes from solutions saturated with hydrochloric acid in which a basic salt would seem to be an impossibility. In view of these apparently conflicting facts, it seems necessary to draw the conclusion that the differences in color exhibited by chromic compounds and their solutions are due to more

* Vide Van Cleeff, J. prakt. Chem., II, xxiii, 58. † Loc. cit.

than one cause, probably to the formation of basic salts in certain cases, and also, in other instances, to a change in water of crystallization which is evidently accompanied by a molecular transformation.

Uranyl Chloride and Cæsium Chloride. — A careful series of experiments with cæsium chloride and uranyl chloride has resulted in the discovery of but a single salt. This compound, $2CsCl.UO_2Cl_2$, corresponds, except that it contains no water, to the previously described salts, $2KCl.UO_2Cl_2.2H_2O$, $2KBr.UO_2Br_2.2H_2O$, $2NH_4Cl.UO_2Cl_2.2H_2O$, and $2NH_4Br.UO_2Br_2.2H_2O$, but some fluorides of other types have been described.

The compound under consideration forms apparently orthorhombic, yellow crystals which are usually small and blade-like in shape. The products used for analysis were made under the following conditions: Crop A, by making a concentrated aqueous solution of 10 g. of cæsium chloride and 50 g. of uranyl chloride, then running in gaseous hydrochloric acid until crystals began to form and cooling; Crop B, by the same method as above, using 50 g. of cæsium chloride and 10 g. of uranyl chloride; Crops C and D, by spontaneous evaporation of solutions containing 50 g. of cæsium chloride and 15 g. of uranyl chloride; and E, by the evaporation of a solution of 15 g. of cæsium chloride and 50 g. of uranyl chloride. The results were as follows:

	Found.					Calculated for $2CsCl.UO_2Cl_2$.
	A.	B.	C.	D.	E.	
Cs . .	39.43	39.63	40.07	. . .	. . .	39.15
UO_2 .	40.37	41.14	40.96	41.85	43.39	39.95
Cl . .	20.63	21.17	20.85	20.84	20.59	20.90

The cæsium chloride used in this investigation was from a liberal supply of cæsium and rubidium salts presented to this laboratory, for the encouragement of scientific research, by Herr E. Merck of Darmstadt, Germany, and we wish to express our sincere thanks to him for his generosity.

SHEFFIELD SCIENTIFIC SCHOOL,
June, 1895.

ON THE AMMONIUM-CUPROUS DOUBLE HALOGEN SALTS.*

By H. L. WELLS and E. B. HURLBURT.

The existence of ammonium-cuprous double halides has long been known, but since no complete investigation of these compounds had been made, a careful study of them has been undertaken.

Mitscherlich † prepared the potassium salt $4KCl.Cu_2Cl_2$, and mentioned the corresponding ammonium salt. This salt, $4NH_4Cl.Cu_2Cl_2$, has been obtained in the present investigation.

Deherain ‡ described three double chlorides, $4NH_4Cl.Cu_2Cl_2.H_2O$, $2NH_4Cl.Cu_2Cl_2$, and $NH_4Cl.Cu_2Cl_2$. The first of these salts, if the molecule of water is omitted, corresponds to the compound mentioned by Mitscherlich which we have obtained, and we are convinced that Deherain's formula for it is wrong. The second salt, $2NH_4Cl.Cu_2Cl_2$, has not been obtained by us, but since it corresponds in type to a bromide and an iodide which are easily prepared, its existence seems possible. The third salt of Deherain, $NH_4Cl.Cu_2Cl_2$, probably does not exist, for we have failed to obtain it, as has Ritthausen also. Ritthausen, § while not being able to prepare $NH_4Cl.Cu_2Cl_2$, obtained the compound $4NH_4Cl.3Cu_2Cl_2$, and we have confirmed this result. The compositions required for the two formulæ do not differ widely, so that it is probable that Deherain analyzed the salt $4NH_4Cl.3Cu_2Cl_2$ and gave it an incorrect formula.

As far as we know, no double bromides have been previously described. Saglier ‖ has described an ammonium-cuprous

* Amer. Jour. Sci., l, 1895.
† Ann. Chim. Phys., lxxiii, 384.
‡ Compt. rend., lv, 808.
§ J. prakt. Chem., lix, 369.
‖ Compt. rend., civ, 1440.

iodide, to which the formula $2NH_4I.Cu_2I_2.H_2O$ is given. The single double iodide which we have obtained corresponds to Saglier's description and to his formula, except that we have found it to be undoubtedly anhydrous.

In the present investigation a great number of experiments have been made, with gradually varying proportions of the constituent salts in each case, in order to obtain as many compounds as possible.

The Chlorides, $4NH_4Cl.Cu_2Cl_2$ and $4NH_4Cl.3Cu_2Cl_2$. — These compounds were prepared by making hot hydrochloric acid solutions of mixtures of the simple salts, usually in the presence of copper wire, and cooling to crystallization. The first salt mentioned above is very readily oxidized by exposure to air; hence it has been found advisable in making it to use a flask and to protect the solution from air by means of a stream of carbonic acid.

The compound $4NH_4Cl.Cu_2Cl_2$ requires the presence of a comparatively large amount of ammonium chloride for its formation, and crystallizes in colorless prisms which rapidly change in color through brown to green upon exposure to the air. Crystals 20 mm. in length and 5 mm. in thickness were observed.

The following analyses of two separate crops were made:

	Found.		Calculated for $4NH_4Cl.Cu_2Cl_2$.
Ammonium	17.91	18.12	17.48
Copper	29.69	29.28	30.79
Chlorine	50.66	50.37	51.73
	98.26	97.77	100.00

It was necessary to dry the samples for analysis very rapidly on account of their instability, and some water was unavoidably left in them, causing the low summations. The amount of water corresponding to one molecule (Deherain's formula) is 4.19 per cent.

The other chloride, $4NH_4Cl.3Cu_2Cl_2$, is produced when the simple salts are mixed in the required proportion in hydrochloric acid solution, and also under considerable variations from these proportions. It forms brilliant, colorless dodecahedra

which are moderately stable in the air at ordinary temperatures, but gradually turn green on exposure.

The following analyses of three separate crops were made:

	Found.			Calculated for $4NH_4Cl.3Cu_2Cl_2$.
	I.	II.	III.	
Ammonium . .	9.39	9.73	9.73	8.92
Copper . . .	47.19	46.73	46.79	47.15
Chlorine . . .	42.81	43.11	43.13	43.93
	99.39	99.57	99.65	100.00

The calculated amounts of ammonium, copper, and chlorine for Deherain's formula, $NH_4Cl.Cu_2Cl_2$, are 7.15, 50.50, and 42.35 respectively, and it does not seem possible that this formula represents the true composition of the salt, because the samples analyzed were well crystallized and evidently very pure.

The Bromides, $4NH_4Br.Cu_2Br_2$ and $2NH_4Br.Cu_2Br_2.H_2O$. — By the use of ammonium bromide, cuprous bromide, hydrobromic acid, and copper wire, these compounds were produced similarly to the chlorides, but since these salts oxidize much less readily than the chlorides, no protection by means of carbon dioxide was necessary in any case.

The first salt, $4NH_4Br.Cu_2Br_2$, is formed in the presence of an excess of ammonium bromide, and resembles the corresponding chloride in form, occurring in long, colorless prisms which turn green after long exposure to the air. Analyses of two separate crops gave:

	Found.		Calculated for $4NH_4Br.Cu_2Br_2$.
	I.	II.	
Ammonium	10.24	10.24	10.61
Copper	18.81	18.47	18.68
Bromine	70.93	70.60	70.71
	99.98	99.31	100.00

The other bromide, $2NH_4Br.Cu_2Br_2.H_2O$, is formed in the presence of a relatively greater amount of cuprous bromide. It forms brilliant, colorless rhombohedra, sometimes 15 mm. long and 9 mm. wide, and it is more stable in the air than the first bromide. Analyses of two separate crops gave:

	Found. I.	Found. II.	Calculated for $2NH_4Br.Cu_2Br_2.H_2O$.
Ammonium	6.88	6.90	7.19
Copper	25.61	25.20	25.32
Bromine	63.76	64.08	63.90
Water (difference) . . .	3.75	3.82	3.59

The Iodide, $2NH_4I.Cu_2I_2$.— Only one double iodide could be obtained by the use of ammonium iodide and cuprous iodide in widely varying proportions in hydriodic acid solutions. This circumstance agrees with the observation made upon several other series of double salts studied in this laboratory, that the number of double salts possible decreases from the chlorides to the iodides. Two separate crops gave the following results upon analysis:

	Found. I.	Found. II.	Calculated for $2NH_4I.Cu_2I_2$.
Ammonium	5.84	5.95	5.36
Copper	18.75	. . .	18.90
Iodine	75.07	75.55	75.74
	99.66		100.00

Summary. — The double salts obtained in the present investigation are as follows:

2 : 1 Type.	1 : 1 Type.	2 : 3 Type.
$4NH_4Cl.Cu_2Cl_2$	. . . . .	$4NH_4Cl.3Cu_2Cl_2$
$4NH_4Br.Cu_2Br_2$	$2NH_4Br.Cu_2Br_2.H_2O$	. . . . .
. . . . .	$2NH_4I.Cu_2I_2$	. . . . .

The two bromides are apparently new compounds, while a formula without water has been given to Saglier's iodide. The compound, $NH_4Cl.Cu_2Cl_2$, of Deherain probably does not exist.

It was hoped that ammonium-cuprous salts of other types, corresponding to the cæsium-cuprous salts described by one of us,* would be found, but such has not been the case, and there

* Amer. Jour. Sci., xlvii, 96.

is no correspondence between the two series. The view advanced in the article just mentioned, that the formula $4NH_4Cl.3Cu_2Cl_2$ might be considered somewhat doubtful on account of its complexity and because its variation from the 1 : 2 type is slight, seems to have been unfounded.

SHEFFIELD SCIENTIFIC SCHOOL,
June, 1895.

ON THE DOUBLE FLUORIDES OF CÆSIUM AND ZIRCONIUM.*

By H. L. WELLS and H. W. FOOTE.

In connection with his comprehensive work on zirconofluorides, Marignac † has investigated the double fluorides of zirconium with ammonium, sodium, and potassium, and since the corresponding cæsium salts have never been investigated, we have undertaken a study of them.

The following table gives Marignac's ammonium and potassium salts, together with those which we have prepared with cæsium:

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.	2 : 3 Type.
$3NH_4F.ZrF_4$	$2NH_4F.ZrF_4$	. . . . .	. . . . .
$3KF.ZrF_4$	$2KF.ZrF_4$	$KF.ZrF_4.H_2O$	. . . . .
. . . . .	$2CsF.ZrF_4$	$CsF.ZrF_4.H_2O$	$2CsF.3ZrF_4.2H_2O$

The analogy between two types of cæsium and potassium salts is complete, while one type varies in each series. No evidence has been found that cæsium, in this case, forms a greater variety of compounds than potassium.

The symmetrical arrangement of the vacancies in the table, where no salts have been discovered, indicates that alkaline fluorides of lower molecular weight combine with a relatively smaller number of molecules of zirconium fluoride, while those of higher molecular weight combine with a greater number of such molecules.

The 2 : 1 type is the only one occurring in all three series. This is the common and usually the only type of double halogen salts formed by tetravalent elements; hence its occurrence in all cases was to be expected. The single sodium salt

* Amer. Jour. Sci., l, 1896.

† Ann. Chim. Phys., III, lx, 257.

described by Marignac, $5NaF.2ZrF_4$, does not correspond to any of the compounds in the above table, but it is to be noticed that the composition corresponding to this formula varies but little from that required for $2NaF.ZrF_4$. Although Marignac's work on this salt was, as usual, very thorough and careful, it seems possible that his products may have been the 2 : 1 salt containing a small amount of some impurity, possibly a 3 : 1 compound.

Marignac described the salts $Mn_2ZrF_8.6H_2O$, $Cd_2ZrF_8.6H_2O$, $Zn_2ZrF_8.12H_2O$, and $Cu_2ZrF_8.12H_2O$, all of which correspond to a 4 : 1 type which has not been obtained with the alkali metals. This type and those given in the preceding table make five varieties of zirconofluorides, one of which has been discovered in the present investigation.

The materials used for the preparation of the cæsium salts under consideration were carefully purified by ourselves. Hydrofluoric acid was made from perfectly pure fluor-spar and sulphuric acid, using a platinum still and redistilling the product. Cæsium carbonate, purified by the method described by one of us,* was used in preparing the fluoride. Zircon was used as the source of zirconium. The crude hydroxide was conveniently obtained by fusing the finely pulverized mineral with four parts of sodium carbonate, treating the resulting mass with hydrochloric acid, evaporating with an excess of sulphuric acid until the latter fumed, taking up with water, filtering and precipitating with ammonia. For purifying the zirconia, the method of Mitchell which has been advocated by Baskerville † was found convenient. This consists in dissolving the zirconium hydroxide in hydrochloric acid, nearly neutralizing with ammonia, adding a strong solution of sulphur dioxide and boiling. The precipitate, which, from the results of Venable and Baskerville,‡ appears to be a basic zirconium sulphite, can readily be washed free from iron.

The double salts were prepared by mixing solutions of the two fluorides in widely varying proportions, in the presence

* Amer. Jour. Sci., xlvi, 188. † Jour. Amer. Chem. Soc., xvi, 475.
‡ Ibid., xvii, 448.

of more or less hydrofluoric acid, evaporating to the proper point, and cooling.

When cæsium fluoride is in excess, even with very small amounts of zirconium fluoride, the salt $2CsF.ZrF_4$, is formed. It crystallizes in rather large, simple hexagonal plates, showing negative double refraction, and it can be recrystallized unchanged from water.

When a larger proportion of zirconium fluoride is used, the salt $CsF.ZrF_4.H_2O$ is obtained. This forms monoclinic crystals elongated in the direction of the *b* axis, and with faces which are usually too rough for accurate measurement. This salt also can be recrystallized unchanged from water.

With a large excess of zirconium fluoride extremely small, difficultly soluble crystals of the salt $2CsF.3ZrF_4.2H_2O$ are produced. The small crystals have a slight action upon polarized light, but their form could not be made out. It does not recrystallize from water in a pure condition, the product being mixed with the 1 : 1 salt.

To determine cæsium and zirconium, the fluorides were converted into sulphates, then zirconium was separated from cæsium by the use of ammonia, and zirconium oxide and cæsium sulphate were finally weighed. In order to determine fluorine a separate portion was dissolved in water, zirconium hydroxide was precipitated with ammonia, sodium carbonate was added in slight excess to the filtrate, and all the ammonia was removed by evaporation. To the hot solution calcium nitrate was added, and the resulting precipitate, after ignition, was cautiously treated with dilute formic acid until, after evaporation on the water-bath, a further addition of the acid produced no effervescence. The calcium fluoride finally remaining after a final evaporation was washed, ignited, and weighed. The results of the fluorine determinations were invariably somewhat low.

The substitution of formic acid for the acetic acid usually used in removing calcium carbonate from the fluoride was suggested by the greater volatility of the first acid and the solubility of its calcium salt. We have found the modification to

be an improvement as far as convenience is concerned, but we are not yet prepared to say that it is more accurate than the old method.

Water was determined by heating the substance in a boat behind a layer of dry sodium carbonate in a combustion tube, and collecting and weighing it in a calcium-chloride tube.

The following analyses of separate crops were made:

$2CsF.ZrF_4$.

	Found.			Calculated.
	A.	B.	C.	
Cæsium	56.41	. . .	55.51	56.60
Zirconium . . .	18.94	19.30	19.16	19.15
Fluorine	22.73	22.75	. . .	24.25
Water	1.63	0.98	0.97	. . .

The small amount of water found in the analyses was evidently mechanically included, for under the microscope bubbles of mother-liquor could be occasionally seen within the crystals.

$CsF.ZrF_4.H_2O$.

	Found.		Calculated.
	A.	B.	
Cæsium	. . .	38.44	39.58
Zirconium . . .	27.19	27.11	26.79
Fluorine	27.24	27.52	28.27
Water	6.27	5.20	5.36

$2CsF.3ZrF_4.2H_2O$.

	Found.		Calculated.
	A.	B.	
Cæsium	32.03	30.56	31.74
Zirconium . . .	32.45	33.48	32.22
Fluorine	31.09	30.43	31.74
Water	4.40	3.96	4.30

SHEFFIELD SCIENTIFIC SCHOOL,
July, 1895.

ON CERTAIN DOUBLE HALOGEN SALTS OF CÆSIUM AND RUBIDIUM.*

By H. L. WELLS and H. W. FOOTE.

1. *The Complicated Rubidium-Antimony Chloride.*

Remsen and Saunders † have described a salt to which they gave the formula $23RbCl.10SbCl_3$ as the most probable one. Wheeler, ‡ working in this laboratory, confirmed Remsen and Saunders' results, and discovered besides an analogous bromide, to which the probable formula $23RbBr.10SbBr_3$ was given. Remsen and Brigham § prepared the salt $23RbCl.10BiCl_3$. Herty ‖ has since described the two potassium salts $23KCl.10SbCl_3$ and $23KBr.10SbBr_3.27H_2O$, and some mixtures of these two salts.

In view of all this work, there can scarcely be a doubt as to the existence of a type of salts with a somewhat complicated ratio, but in view of the fact that this complicated ratio 23 : 10 is apparently an exception to the simplicity of composition of all other carefully investigated double halogen salts, the subject seemed worthy of some further investigation. For the purpose we have studied only the rubidium-antimony chloride of Remsen and Saunders, as this salt is readily prepared and is capable of repeated recrystallization from hydrochloric acid solution.

The possibility suggested itself that the product might consist of two simpler salts of similar or identical crystalline form, which were capable of crystallizing together, and that previous investigators had made use of conditions which resulted in obtaining a constant mixture of two such salts. Although

* Amer. Jour. Sci., III, 1897.
† Ibid., xiv, 155.
‡ Ibid., xlvi, 269.
§ Amer. Chem. Jour., xiv, 174.
‖ Ibid., xvi, 490.

this supposition had scarcely any probability in view of the existence also of the rubidium-antimony bromide and of the two potassium salts, we have put the question to test by repeatedly recrystallizing the salt, using not only ordinary dilute hydrochloric acid for this purpose, but also more dilute and much more concentrated acid and also an alcoholic hydrochloric acid solution. As will be seen from the analyses, given beyond, no variation in composition could be detected by the use of these widely varying solvents for recrystallization, and it therefore appears impossible that the salt can be a mixture.

As a starting-point, we used a solution in hydrochloric acid containing the constituents RbCl and $SbCl_3$ in the exact molecular proportion 23 : 10. Product A was the first, B the third, and C the fifth recrystallization from pure dilute hydrochloric acid. The product D was obtained by adding concentrated hydrochloric acid to a nearly saturated warm solution of the salt in dilute hydrochloric acid. E was obtained from a very strong hydrochloric acid solution formed by passing a rapid current of hydrogen chloride gas into the solution as it cooled. F was obtained by recrystallizing the salt from hydrochloric acid, which was kept as dilute as it could be without producing the basic double salt to be described beyond. G was a product obtained by recrystallizing the salt from a mixture of equal volumes of dilute hydrochloric acid and alcohol.

The two products obtained from concentrated hydrochloric acid solution had a pale yellow color, while the others were all white. The crystals were usually well-formed six-sided plates which showed no definite optical properties.

The analyses of the various products are as follows:

	Rubidium.	Antimony.	Chlorine.
A	39.23	23.85	37.01
B	39.23	23.84	36.99
C	. . .	23.91	. . .
D	39.25	23.98	. . .
E	39.31	23.89	. . .
F	39.03	23.86	. . .
G	39.11	23.90	. . .
Average	39.19	23.89	37.00

Method of Analysis. — For the determination of antimony and rubidium, a portion of about half a gram was dissolved in water and enough hydrochloric acid to prevent antimony oxychloride from precipitating. The solution was heated to boiling and hydrogen sulphide passed in. The solution was then cooled and the antimony sulphide filtered on a Gooch crucible and washed with water and with alcohol. The crucible was then slowly heated to 230° and cooled in an oven filled with carbonic acid. The precipitate was weighed as Sb_2S_3. The filtrate containing rubidium was evaporated with sulphuric acid, and the residue ignited in a stream of air containing ammonia and weighed as Rb_2SO_4. Chlorine was determined by dissolving a separate portion in water acidified with tartaric and nitric acids and precipitating with silver nitrate. This was allowed to stand for some time, and the precipitate was then collected on a Gooch crucible and weighed. The methods used are almost identical with those of Wheeler.

The accuracy of the antimony determination was checked in the following manner. The salt $Cs_3Sb_2Cl_9$ was prepared from very pure materials and carefully recrystallized, and antimony determined by the above method. The per cent of antimony is nearly the same as in the rubidium antimony salt under consideration. The following results were obtained:

	I.	II.	III.	IV.
Per cent Sb found . .	25.37	25.42	25.43	25.44
" " calculated .	25.13	. . .	. . .	. . .

The atomic weights used in all the calculations were Rb, 85.43; Sb, 120.43; Cl, 35.45; S, 32.07; Ag, 107.92; Cs, 132.89.

Since the method used for the determination of antimony gives results which are slightly too high, we believe that a deduction of the average error 0.25 per cent from the antimony found in the analyses of the rubidium salt will give a result which is nearer the truth.

	Rb.	Sb.	Cl.
Average previously given . .	39.19	23.89	37.00
Average with correction for Sb	39.19	23.64	37.00
Calculated for $Rb_{23}Sb_{10}Cl_{53}$ . .	38.92	23.86	37.22
Calculated for $Rb_7Sb_3Cl_{16}$ . .	39.18	23.66	37.16

It may be noticed that the results agree rather more satisfactorily with the formula $7RbCl.3SbCl_3$ than with the more complicated one advanced by Remsen and Saunders. The differences between these formulæ are, however, so slight that it is probably entirely impossible to decide between them by means of chemical analysis, the ratio Rb : Sb being 230 : 100 in one case, and in the other 233 : 100. However, since it is customary to use the simplest applicable formula for a chemical compound, we propose the formula $7RbCl.3SbCl_3$ for this salt and corresponding formulæ for other salts of this series. Herty's hydrous salt, to which he gave the formula $23KBr.10SbBr_3.27H_2O$, agrees well with the formula $7KBr.3SbBr_3 8H_2O$. It must be admitted that the 7 : 3 ratio is an unusually complicated one, but it is far simpler than 23 : 10, and is scarcely a marked exception to the general simplicity of double halogen salts.

2. *A Rubidium-Antimony Oxychloride,* $2RbCl.SbCl_3.SbOCl$.

In attempting to recrystallize the salt $7RbCl.3SbCl_3$ from very dilute hydrochloric acid, just enough to prevent the formation of antimony oxychloride, this new salt was obtained in the form of short colorless prisms possessing a rather high lustre. It can be recrystallized from very dilute hydrochloric acid.

The following results were obtained from analyses of separate crops:

	Found.		Calculated for $2RbCl.SbCl_3.SbOCl$.
	I.	II.	
Rb	26.54	26.68	26.68
Sb	37.58	37.36	37.61
Cl	32.75	32.80	33.21
O (by diff.) . . .	3.13	3.16	2.50

It is interesting to notice that Benedict* has described the potassium salt $2KCl.SbCl_3.SbOCl$, which corresponds exactly to this rubidium compound.

3. *The Cæsium-Bismuth Chlorides and Iodides.*

The double chlorides of bismuth with cæsium have been described by Remsen and Brigham.† These authors did not

* Proc. Amer. Acad., xxix, 212. † Amer. Chem. Jour., xiv, 179.

state, however, how widely the conditions had been varied, and we have repeated the work, varying the proportions of cæsium and bismuth as much as possible, and have found exactly the same salts as described by them. These salts are,

$3CsCl.BiCl_3$
$3CsCl.2BiCl_3$

$3CsCl.BiCl_3$. — This salt forms in colorless plates when 50 g. of cæsium chloride are mixed in hydrochloric acid solution with from 1–25 g. of bismuth chloride. The analyses were made on samples, dried but a short time in the air, which apparently contained a little mechanically included water. The following results were obtained:

	Found. I.	Found. II.	Calculated for $3CsCl.BiCl_3$.
Bi	24.80	24.47	25.36
Cs	47.94	. . .	48.66
Cl	. . .	. . .	25.98

$3CsCl.2BiCl_3$. — When 50 g. of bismuth chloride are mixed with from 1–80 g. of cæsium chloride, the salt $3CsCl.2BiCl_3$ crystallizes in light yellow needles, sometimes broadened and looking like plates and again much shorter and thicker.

The following analyses were made:

	Found. I.	Found. II.	Calculated for $3CsCl.2BiCl_3$.
Bi	36.99	36.58	36.67
Cs	34.69	34.94	35.17
Cl	. . .	. . .	28.16

$3CsI.2BiI_3$, Cæsium-Bismuth Iodide.

We could obtain only one double iodide of bismuth and cæsium, although the proportions of cæsium and bismuth were varied greatly. The salt formed as a crystalline precipitate, difficultly soluble especially in an excess of cæsium iodide, when 1 g. of bismuth iodide was added to 50 g. of cæsium iodide and when 1 g. of cæsium iodide was added to 50 g. of bismuth iodide. With an excess of cæsium, the color was a bright red, while with an excess of bismuth the color was more of a reddish brown.

Methods of Analysis. — The methods here given were used in both the double chlorides and iodide of bismuth.

Halogens were determined as the silver salts being precipitated from a solution acidified with tartaric and nitric acids and, after standing, filtered and weighed on a Gooch crucible. As Remsen and Brigham had mentioned a difficulty in determining bismuth, we made a few determinations of it in Bi_2O_3, which was made by precipitating $BiONO_3$ with water from a nitric acid solution of $Bi(NO_3)_3$, and heating the precipitate to constant weight in a platinum dish. The method finally adopted was to dissolve the substance in water slightly acidified with hydrochloric acid and precipitate Bi_2S_3 from the cold solution with hydrogen sulphide. The precipitate was filtered and immediately dissolved in nitric acid and digested for some time on the water bath until completely decomposed. The sulphur was filtered off and the filtrate, diluted to about 300–400 c. c., was heated and ammonium carbonate added in slight excess. It was placed on the water bath for an hour or two, until the liquid had become nearly clear and the excess of ammonium carbonate had been driven off, and it was then filtered on a Gooch crucible and ignited strongly over a Bunsen burner and weighed as Bi_2O_3.

Two determinations on Bi_2O_3 gave the following results:

I Amt. Bi_2O_3 taken = 0.1979 g. Amt. Bi_2O_3 found = 0.1974 g.
II " " " = 0.3604 g. " " " = 0.3617 g.

The filtrate from the bismuth precipitation was evaporated with sulphuric acid and ignited in a stream of air containing ammonia. The residue was weighed as Cs_2SO_4.

The results obtained from the analysis of the double iodide were as follows:

	Found. I.	Found. II.	Calculated for $Cs_3Bi_2I_9$.
Bi	21.34	21.15	21.25
Cs	20.75	20.31	20.38
I		58.02	58.37

SHEFFIELD CHEMICAL LABORATORY,
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ON THE DOUBLE FLUORIDES OF ZIRCONIUM WITH LITHIUM, SODIUM, AND THALLIUM.*

By H. L. WELLS and H. W. FOOTE.

In a previous article † we have described the cæsium-zirconium fluorides, and upon comparing these with the corresponding ammonium and potassium salts, which had been previously described by Marignac, ‡ it was observed that the types of salts formed varied with the molecular weights of the alkaline fluorides in an interesting manner. The fluorides of smaller molecular weight gave types with a larger relative number of these molecules, while the fluorides of higher molecular weights combined with more zirconium fluoride than the others. This relation is made clear from the following table, which was given in the previous article referred to:

3 : 1 Type.	2 : 1 Type.	1 : 1 Type.	2 : 3 Type.
$3NH_4F.ZrF_4$	$2NH_4F.ZrF_4$	. . . .	. . . . .
$3KF.ZrF_4$	$2KF.ZrF_4$	$KF.ZrF_4$	. . . . .
. . . . .	$2CsF.ZrF_4$	$CsF.ZrF_4$	$2CsF.3ZrF_4.2H_2O$

The present investigation was undertaken with the view, in the first place, of testing the apparent rule with lithium fluoride, which has a lower molecular weight than the fluorides previously experimented upon. Our expectations were realized by the preparation of the salt $4LiF.ZrF_4.\frac{2}{3}H_2O$. The salt $2LiF.ZrF_4$ was also obtained, but, in spite of a careful search, no intermediate 3 : 1 salt could be discovered. The following table, giving the lithium, potassium, and cæsium salts, shows a perfectly symmetrical gradation in types according to the

* Amer. Jour. Sci., III, 1897. † Ibid., IV. i, 18.
‡ Ann. Chim. Phys., ix, 257.

atomic weights of the alkali metals, except that the intermediate lithium salt is missing.

Type.	Lithium Salts.	Potassium Salts. (Marignac.)	Cæsium Salts.
4 : 1	$4LiF.ZrF_4.\frac{2}{3}H_2O$	. . . . .	. . . . .
3 : 1	. . . . .	$3KF.ZrF_4$	. . . . .
2 : 1	$2LiF.ZrF_4$	$2KF.ZrF_4$	$2CsF.ZrF_4$
1 : 1	. . . . .	$KF.ZrF_4.H_2O$	$CsF.ZrF_4.H_2O$
2 : 3	. . . . .	. . . . .	$2CsF.3ZrF_4.2H_2O$

Marignac's two ammonium salts, 3 : 1 and 2 : 1, also enter the series symmetrically.

We have investigated also the thallous-zirconium fluorides, since the high atomic weight of thallium led us to expect that it would possibly yield a series of salts symmetrical with those of the alkali metals with a still higher ratio of zirconium than was the case with cæsium. Such was not the case, however. The salts discovered were:

$3TlF.ZrF_4$, $5TlF.3ZrF_4.H_2O$, $TlF.ZrF_4$, and $TlF.ZrF_4.H_2O$.

Two of these three types of thallous salts correspond to types of alkali-metal salts, while one type, the 5 : 3, is a new one, but the series is not symmetrical with the others according to the atomic weights.

Since Marignac had described but one sodium-zirconium fluoride, $5NaF.2ZrF_4$, and since this differs from all other alkaline zirconium fluorides, we have undertaken a new investigation of the sodium salts. As a result, we have fully confirmed Marignac's results as to the 5 : 2 salt, which is the one most readily obtained, and we have succeeded in preparing a new salt, $2NaF.ZrF_4$, which corresponds to the most usual type of double halogen salts of tetravalent elements. It is evident, however, that the sodium salts, like those of thallium, do not form a symmetrical series with the others.

The following table gives a list of the sodium and thallium salts, and shows the positions, "X," of the other compounds prepared by Marignac and ourselves.

Type.	Lithium Salts.	Ammonium Salts. (Marignac)	Sodium Salts.	Potassium Salts. (Marignac)	Cæsium Salts.	Thallium Salts.
4 : 1	X	..	.....	..	..	.....
3 : 1	..	X	.....	X	..	$3TlF.ZrF_4$
5 : 2	..	..	$5NaF.2ZrF_4$	..	..	.....
2 : 1	X	X	$2NaF.ZrF_4$	X	X	.....
5 : 3	..	..	.....	..	..	$5TlF.3ZrF_4H_2O$
1 : 1	..	..	.....	X	X	$TlF.ZrF_4$ / $TlF.ZrF_4.H_2O$
2 : 3	..	..	.....	..	X	.....

While our investigation has shown that the rule for the variation of the types with the atomic weights applies only partially to the zirconium double fluorides, we have shown at least that the variety of types is remarkable, and it is also noticeable that the ratios are nearly the simplest that can exist in such number between the extreme limits 4 : 1 and 2 : 3.

Preparation. — Thallium fluoride was prepared by dissolving the metal in sulphuric acid, adding an excess of baryta water, filtering and passing carbonic acid into the hot solution. The filtrate from this precipitation was evaporated and treated with hydrofluoric acid in excess. The salts were prepared by mixing the acid solutions of the fluorides in varying proportions, evaporating and cooling to crystallization. The salts were then removed and pressed between filter papers till dry. In all cases they were stable in the air.

Method of Analysis. — Zirconium and the alkalies were determined by evaporating the salt with sulphuric acid to drive off hydrofluoric acid, precipitating zirconium hydroxide with ammonia and weighing ZrO_2. The filtrate was evaporated to dryness and the alkali determined as sulphate, either by igniting with ammonium carbonate or heating in a current of air containing ammonia. When thallium was present, the fluoride was dissolved in water, a little sulphurous acid added to make sure that the thallium was all in the univalent condition, and the zirconium precipitated with ammonia. The precipitate needed to be very thoroughly washed. The filtrate was evaporated nearly or quite to dryness to remove free

ammonia, diluted to a volume of about 100 c. c., heated to boiling and potassium iodide added in excess to precipitate thallium iodide. This was collected on a Gooch crucible, washed with eighty per cent alcohol, dried at 100° C. and weighed. Fluorine was determined by the ordinary calcium fluoride method after precipitating zirconium with ammonia and removing ammonium salts by evaporation with sodium carbonate. Water was determined by heating the salt in a combustion tube behind a layer of dry sodium carbonate and collecting the water in a calcium chloride tube.

Salts of Lithium.

$2LiF.ZrF_4$. — This salt forms when from 0.7 g. to 2 g. of lithium fluoride are added to 20 g. of zirconium fluoride. The crystals are hexagonal, showing prism and pyramid and rarely a basal plane. In appearance, they are very much like crystals of quartz from Herkimer County, New York, but they are very small. On recrystallizing, the 4 : 1 salt was formed.

Separate crops were analyzed with the following results:

	Found. I.	Found. II.	Calculated for Li_2ZrF_6.
Li	6.03	6.39	6.42
Zr	41.81	41.64	41.28
F		51.62	52.30

$4LiF.ZrF_4.\frac{2}{3}H_2O$. — This was the most unsatisfactory salt obtained, though it seems undoubtedly to establish the 4 : 1 type. As lithium fluoride is very insoluble, only a comparatively small amount could be dissolved in zirconium fluoride, and apparently we could not go far enough toward the lithium end to get the salt in pure condition. It formed in a crust ordinarily, and the crystals were very small. Under the microscope, no mixture with another salt could be found in the crops analyzed. Once, however, it was obtained mixed with the 2 : 1 salt, as seen under the microscope, showing there could probably be no intermediate salt. Various conditions were tried, and crops were obtained from both hot and cold

solutions. It forms when 5 to 7 g. of lithium fluoride are mixed with 20 g. of zirconium fluoride. On recrystallizing, lithium fluoride is precipitated.

Following are the results of the analyses:

	Li.	Zr.	H_2O.	F.
I	9.54	33.14	4.83	. . .
II	. . .	. . .	4.93	. . .
III	9.79	33.30	4.35	53.16
IV	. . .	33.23	. . .	. . .
V	. . .	33.02	. . .	. . .
Calculated for $Li_4ZrF_8.\frac{2}{3}H_2O$	9.93	31.91	4.26	53.90

Salts of Sodium.

$2NaF.ZrF_4$. — This salt crystallizes in very minute crystals of hexagonal outline, coming down in a crust when from one to two parts of sodium fluoride are added to fourteen parts of zirconium fluoride. The salt does not recrystallize. The following results were obtained from separate crops. The water was probably mechanically included.

	Found. I.	Found. II.	Calculated for Na_2ZrF_6
Na	18.66	18.41	18.40
Zr	34.78	36.21	36.00
H_2O	1.96	0.50	. . .
F*	44.60	44.88	45.60

$5NaF.2ZrF_4$. — Marignac has previously described this salt, which comes down under wide conditions in very good crystals and recrystallizes easily. Prof. L. V. Pirsson has kindly examined the crystals and made the following report:

"The crystals show good sharp forms, but are very small. They appear distinctly orthorhombic in habit, consisting in the main of rather stout prisms, made up of two prismatic planes, *m* and *m'*, and terminated by a rather steep brachydome. In another habit, which is rarer, the front pinacoid, *a*, is broadly developed, while the prisms are very small; this type also shows at times a pyramid, *p*. The plane of the optic axes lies

* By difference.

in the base and $a = \mathfrak{c}, b = \mathfrak{a}, c = \mathfrak{b}$. The optic angle is large, and it could not be told whether a or b was the acute bisectrix. The double refraction is very low. The crystals in their form strongly recall the figures of chrysolite (olivine) shown in the mineralogies."

The analyses gave the following results from different crops:

	Found. I.	Found. II.	Calculated for $Na_5Zr_2F_{13}$.
Na	21.15	21.09	21.23
Zr	33.63	33.55	33.22
F*	45.22	45.36	45.57

Salts of Thallium.

$TlF.ZrF_4.H_2O$ and $TlF.ZrF_4$. — These salts crystallize in somewhat concentrated solutions when one part of thallium fluoride is mixed with three or four parts of zirconium fluoride. The analyses invariably show an excess of zirconium fluoride. The hydrous salt crystallizes in needles, if the solution be cooled before precipitation occurs. If the solution is evaporated until crystals begin to form and then cooled, the anhydrous salt deposits in minute square plates. The salt gives the 5 : 3 type on recrystallizing. The following results were obtained:

	Found. I.	Found. II.	Calculated for $TlZrF_5.H_2O$.
Tl	48.43	47.91	50.05
Zr	22.93	23.16	22.15
F	. . .	23.17	23.37
H_2O	3.89	4.80	4.43
			Calculated for $TlZrF_5$.
Tl	50.16	49.91	52.37
Zr	23.86	24.08	23.17
F	. . .	24.32	24.46

$5TlF.3ZrF_4.H_2O$. — This salt crystallizes in needles when from one to three and one-half parts of thallium fluoride are added to one part of zirconium fluoride. When about four

* By difference.

parts of thallium fluoride are added, the same salt crystallizes in a different habit, forming prisms of hexagonal outline which under the microscope are seen to be twinned, resembling in this respect the hexagonal-shaped crystals of aragonite. On recrystallizing, both habits give the needle-shaped crystals.

The following analyses were made of the two kinds of crystals. A rather large number of determinations was made on account of the existence of two different forms.

	Tl.	Zr.	H_2O.	F.
I	61.58	16.88	...	...
II	62.05	16.84	...	...
III	61.37	17.14	1.40	...
IV	61.58	16.88	1.17	19.31
V	61.74	17.04	1.42	...
VI	...	...	1.31	...
VII	62.91	16.42	...	...
Calculated for $Tl_5Zr_3F_{17}.H_2O$	62.47	16.58	1.11	19.84

$3TlF.ZrF_4$. — Crystals of this salt form in brilliant octahedra when one part of zirconium fluoride is added to from four to twenty parts of thallium fluoride. It is easily recrystallized.

The following analyses were made:

	Found.		Calculated for Tl_3ZrF_7.
	I.	II.	
Tl	72.82	73.20	73.24
Zr	10.91	10.38	10.80
F	15.65	...	15.96

SHEFFIELD CHEMICAL LABORATORY,
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ON THE CÆSIUM ANTIMONIOUS FLUORIDES AND SOME OTHER DOUBLE HALIDES OF ANTIMONY.

By H. L. WELLS and F. J. METZGER.

We have made a thorough study of the double salts formed by cæsium fluoride and antimonious fluoride with the result that five compounds have been prepared. This is an unusual number for a series of double salts, and it gives a good illustration of the facility with which cæsium forms such compounds.

The salts to be described have the following formulas:

Type.	
1 : 3	$CsF.3SbF_3$
1 : 2	$CsF.2SbF_3$
4 : 7	$4CsF.7SbF_3$
1 : 1	$CsF.SbF_3$
2 : 1	$2CsF.SbF_3$

The previously described antimonious double fluorides, all of which were prepared by Flückiger,* are as follows:

Type.			
1 : 1	$KF.SbF_3$	....	....
2 : 1	$2KF.SbF_3$	$2LiF.SbF_3$	$2NH_4F.SbF_3$
3 : 1	$3NaF.SbF_3$	....	....

The following chlorides, bromides, and iodides have been described:

* Pogg. Ann., lxxxvii, 245 (1852).

Type.	
1 : 2	$RbCl.2SbCl_3$*
3 : 4	$3NH_4I.4SbI_3.9H_2O$ †
1 : 1	$NH_4Cl.SbCl_3$; ‡ $NH_4I.SbI_3.2H_2O$; § $KI.SbI_3H_2O$; § $RbCl.SbCl_3$ ‖
3 : 2	$3KI.2SbI_3.3H_2O$; † $3NaI.2SbI_3.12H_2O$; † $3NH_4I.2SbI_3.3H_2O$ † $3RbCl.2SbCl_3$; * $3RbBr.2SbBr_3$; * $3RbI.2SbI_3$; * $3CsCl.2SbCl_3$¶
2 : 1	$2NH_4Cl.SbCl_3$; ‡ $2NH_4Cl.SbCl_3.H_2O$; ¶ $2KClSbCl_3$; †† $2KCl.SbCl_32H_2O$ ‡‡
7 : 3 §§	$7RbCl.3SbCl_3$; ‖ $7RbBr.3SbCl_3$; * $7KCl.3SbCl_3$; ‖‖ $7KBr.3SbBr_3.8H_2O$ ‖‖
3 : 1	$3NH_4Cl.SbCl_3.1\frac{1}{2}H_2O$; ** $(3KCl.SbCl_3)$; ** $3NaCl.SbCl_3$**
4 : 1	$4NH_4I.SbI_3.3H_2O$†

Upon comparing the cæsium double fluorides with the salts already known, it is to be noticed that two types of the former, 1 : 3 and 4 : 7, do not occur among the latter, and that the 3 : 4, 3 : 2, 7 : 3, 3 : 1, and 4 : 1 types were not found among the cæsium antimonious fluorides. The absence of a 3 : 2 fluoride is remarkable, since the salt $3CsCl.2SbCl_3$ is very sparingly soluble, and because this is a very prominent type among the chlorides, bromides, and iodides. It is evident that a close relation does not exist between the cæsium antimonious fluorides and the other antimonious double halides, and that the types of the former could not have been predicted from a consideration of the latter. In range, the

* Wheeler, Amer. Jour. Sci., (III), xlvi, 269.

† Schäffer, Pogg. Ann., cix, 611.

‡ Deherain, Compt. rend., lii, 734.

§ Nicklès, Ibid., li, 1097.

‖ Remsen and Saunders, Amer. Chem. Jour., xlv, 152.

¶ Setterberg, Öfversigt K. Vetensk-akad. Förhandl., 1882, 23; Remsen and Saunders, loc. cit.

** Poggiale, Compt. rend., xx, 1180. It is probable according to Herty, Amer. Chem. Jour., xv, 81, that $3KCl.SbCl_3$ does not exist.

†† Jacquelaine; Poggiale, loc. cit.; Benedict, Proc. Amer. Acad., xxix, 212.

‡‡ Benedict, loc. cit.

§§ This type was described as 23 : 10; see Wells and Foote, Amer. Jour. Sci., iii, 461.

‖‖ Herty, loc. cit.

cæsium double fluorides extend farther at the antimony end than the others, while they do not extend as far at the alkali-metal end of the series of types.

When all the types of antimonious double halides are considered, they are remarkable for their large number, ten. This number is probably greater than is the case with any other negative element. The types, 1 : 3, 1 : 2, 4 : 7, 3 : 4, 1 : 1, 3 : 2, 2 : 1, 7 : 3, 3 : 1, and 4 : 1, with two or three exceptions, are the simplest that can exist in such number between the two extremes, and arithmetically they extend almost as far in one direction as the other.

Method of Preparation. — Solutions of cæsium fluoride and antimonious fluoride were prepared by treating cæsium carbonate and antimonious oxide, each with an excess of pure hydrofluoric acid. To the antimonious solution the cæsium salt was gradually added in small quantities, and after each addition the liquid was evaporated and cooled until crystallization took place. If a homogeneous product was obtained a portion was removed for analysis, and the process was continued until finally the liquid contained a very large excess of cæsium fluoride. In every case the products were carefully inspected to make sure that they were not mixtures, and at least two crops of a salt were always prepared under somewhat different conditions, and were shown by analysis to be identical in composition before they were accepted as true compounds.

Method of Analysis. — The crystals were carefully dried by pressing between filter papers, and the portions to be analyzed were preserved in glass weighing-tubes which were coated within with a very thin layer of paraffine. For the determination of antimony and cæsium a portion was heated in a platinum crucible with concentrated sulphuric acid until all the hydrofluoric acid was removed, the residue was dissolved in hydrochloric acid, antimony was precipitated as sulphide, collected on a Gooch crucible and weighed after drying in a small oven containing carbon dioxide. Cæsium was weighed as normal sulphate. Fluorine was determined

by converting it into silicon fluoride, collecting the latter in water, and titrating with sodium hydroxide, according to a modification of Offermann's method. The results of these fluorine determinations were invariably somewhat too low, as we found by testing the method with pure potassium silicon fluoride; hence the chief value of these determinations consist in showing that the salts under investigation were not oxy-compounds.

1 : 2 Cæsium Antimonious Fluoride, $CsF.2SbF_3$. — This salt was obtained in the form of beautiful transparent needles by adding 2 or 3 g. of cæsium fluoride to a solution of about 50 g. of antimonious fluoride in somewhat dilute hydrofluoric acid solution, heating to boiling and cooling. Two separate crops gave the following results upon analysis:

	Calculated for $CsSb_2F_7$.	Found.	
		I.	II.
Cæsium	26.28	26.44	. . .
Antimony	47.43	47.36	47.42
Fluorine	26.28	25.23	. . .

1 : 3 Cæsium Antimonious Fluoride, $CsF.3SbF_3$. — This salt crystallizes in the form of stout, transparent prisms. It was obtained by evaporating the mother-liquors from the preceding compound and cooling, or by the use of somewhat less cæsium fluoride in proportion to the antimonious fluoride in a more concentrated solution. Two crops gave the following results:

	Calculated for $CsSb_3F_{10}$.	Found.	
		I.	II.
Cæsium	19.47	17.81	17.60
Antimony	52.71	52.95	53.89
Fluorine	27.82	27.01	26.84

The rather wide variation of the results from the calculated quantities is probably due to the fact that the crystals were taken from a very concentrated antimonious fluoride solution and were consequently not quite pure, even after careful drying on paper.

4 : 7 Cæsium Antimonious Fluoride, $4CsF.7SbF_3$. — This salt crystallizes in transparent plates, and is formed in the presence of a little larger proportion of cæsium fluoride than the preceding compounds. It was obtained, for instance, upon adding about 4 g. of cæsium fluoride to a mother-liquor from the last salt and crystallizing by cooling. Two crops gave the following results:

	Calculated for $Cs_4Sb_7F_{25}$.	Found. I.	Found. II.
Cæsium	28.80	28.99	. . .
Antimony	45.47	46.02	46.03
Fluorine	25.73	24.58	24.61

We cannot say that we are absolutely sure about the formula of this apparently complicated double salt. It cannot be a 1 : 2 compound, for not only is it entirely distinct in appearance from $CsF.2SbF_3$, but coming as it does from a strong antimony solution, the results would naturally come too high rather than too low for antimony. The results vary too widely from a 2 : 3 ratio to make that probable, but they approach somewhat more closely the 3 : 5 ratio. The following calculations will show that we have selected the most probable formula:

	Calculated for $Cs_2Sb_3F_{11}$.	Calculated for $Cs_3Sb_5F_{18}$.	Calculated for $CsSb_2F_7$.
Cæsium	31.86	29.75	26.28
Antimony	43.11	44.75	47.43
Fluorine	25.03	25.50	26.28

1 : 1 Cæsium Antimonious Fluoride, $CsF.SbF_3$. — In the presence of still greater proportions of cæsium fluoride this salt is produced by cooling the properly concentrated solution. It forms square prisms, the ends of which are not usually modified by any planes. Three crops gave the following analyses:

	Calculated for $CsSbF_4$.	Found. I.	Found. II.	Found. III.
Cæsium . . .	40.43	41.44	41.19	. . .
Antimony . .	36.47	35.85	35.66	35.52
Fluorine. . .	23.10	22.30	. . .	. . .

2 : 1 Cæsium Antimonious Fluoride, $2CsF.SbF_3$. — This salt is formed under a wide range of conditions when cæsium fluoride is present in large excess in comparison with the antimonious fluorine. It crystallizes in apparently rhombic prisms, which are often somewhat flattened. Four crops, made under very different conditions, gave the following results:

	Calculated for Cs_2SbF_5.	Found.			
		I.	II.	III.	IV.
Cæsium . .	55.30	54.81	. . .	. . .	. . .
Antimony .	24.95	24.72	24.59	24.92	24.64
Fluorine . .	19.75	19.42	. . .	. . .	. . .

By the use of very concentrated cæsium fluoride solutions with comparatively small amounts of antimonious fluoride, no evidence was obtained of the existence of any double salts containing more cæsium fluoride than the one just described.

Cæsium Antimonious Iodide, $3CsI.2SbI_3$. — It appears that no compound of cæsium iodide with antimonious iodide has been described. The sparingly soluble chloride, $3CsCl.2SbCl_3$ is well known, and this was the only double chloride that Remsen and Saunders * were able to prepare, although four rubidium antimonious chlorides are known. It is evident that the slight solubility of cæsium antimonious chloride makes it impossible to prepare concentrated solutions of the component chlorides, and consequently prevents the formation of salts of other types. We have found that an iodide which corresponds in composition to the chloride can be readily prepared. It is sparingly soluble in hydriodic acid solutions, and it exists in two distinct forms, one of which is brick-red and apparently octahedral in form, while the other is yellow and occurs in thin hexagonal plates. The octahedral salt was prepared by mixing antimonious iodide and cæsium iodide in rather strong hydriodic acid solutions, while the yellow hexagonal salt was made in much less strongly acid solutions, particularly upon diluting them with water, boil-

* Loc. cit.

ing, and cooling. Two crops of each form were analyzed as follows:

	Calculated for $Cs_3Sb_2I_9$.	Found.			
		Red Salt.		Yellow Salt.	
		I.	II.	I.	II.
Cæsium . .	22.39	23.46	. . .	22.15	. . .
Antimony .	13.47	13.91	13.19	14.36	14.52
Iodine . . .	64.14	62.98	. . .	63.03	. . .

This was the only double iodide that we were able to obtain. There is little doubt that a corresponding bromide exists, for we observed, while engaged in work with another object in view, that a yellow precipitate is produced when the bromides of cæsium and trivalent antimony are brought together in solution. Having overlooked the fact that the compound had not been described, we neglected to analyze the product.

Cæsium Antimonic Halides. — So little is known concerning the double halides of quinquivalent elements that it seemed desirable to study the cæsium antimonic compounds. Setterberg * has described a single double chloride, $CsCl.SbCl_5$, and we have confirmed his result, but by using widely varying conditions we have been unable to prepare any other compound. Setterberg's salt crystallizes in long, colorless, transparent needles. A crop of it gave the following results upon analysis:

	Calculated for $CsSbCl_6$.	Found.
Cæsium	28.54	29.14
Antimony	25.75	26.43
Chlorine	45.70	43.94

We have extended our investigation to antimonic fluoride and cæsium fluoride, but the results were disappointing from the the fact that we were able to prepare but one double salt, while Marignac† has described two potassium antimonic fluorides. Either cæsium in this case unexpectedly fails to show as great a tendency to form double salts as does potassium, or else we have failed to find the proper conditions for producing them.

* Loc. cit.

† Liebig's Ann., cxlv, 237.

The salt obtained by us apparently contains hydroxyl, although prepared in strong hydrofluoric acid solutions, and has the formula $CsF.SbF_4OH$. It crystallizes on cooling warm, rather concentrated solutions in the form of bundles of transparent needles. Two crops gave the following analyses:

	Calculated for $CsSbF_5OH$.	Found.	
		I.	II.
Cæsium	36.44	37.77	. . .
Antimony	32.87	31.82	31.72
Fluorine	26.03	25.54	26.18
Hydroxyl	4.66	(4.87)	. . .

SHEFFIELD SCIENTIFIC SCHOOL,
April, 1901.

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ON THE DOUBLE CHLORIDES OF CÆSIUM AND THORIUM.

By H. L. WELLS and J. M. WILLIS.

Nearly all of the known double halogen salts of quadrivalent metals belong to a single type, of which $2KCl.PtCl_4$ and $2KF.SiF_4$ are examples. It has been shown, however, by Marignac* and by Wells and Foote† that the double fluorides of zirconium exist in a variety of types. Therefore, since thorium is somewhat closely related to zirconium, we have undertaken an investigation of some thorium double halides, and have selected the cæsium salts as being the most promising.

Upon attempting to prepare cæsium thorium fluorides we found that thorium fluoride is practically insoluble even in concentrated solutions of cæsium fluoride containing hydrofluoric acid. There is no doubt that the two fluorides combine under these circumstances, but, since we obtained only finely divided precipitates as products and there was no certainty as to their purity, further work on the fluorides was abandoned. Chydenius‡ has previously described two potassium thorium fluorides, $2KF.ThF_4.4H_2O$ and $KF.ThF_4.\frac{1}{2}H_2O$, but on account of the insolubility of thorium fluoride and of these double salts it is probable that there may be some doubt in regard to the correctness of these formulas.

We have prepared two cæsium thorium chlorides, to which we assign the formulas $3CsCl.ThCl_4.12H_2O$ and $2CsCl.ThCl_4.11H_2O$. The amount of water of crystallization in these compounds is somewhat uncertain, since they form very small hygroscopic crystals, and it is difficult to dry them by pressing

* Amer. Chim. Phys., III, lx, 257.
† Amer. Jour. Sci., IV, i, 18; iii, 466.
‡ Pogg. Ann., cxix, 43.

on paper. The search for double chlorides was made systematically by starting with a solution of about 65 g. of thorium chloride in hydrochloric acid, adding 2 to 4 g. of cæsium chloride at a time, and evaporating and cooling after each addition, until finally, after dividing the solution and using a part of it, a very large excess of cæsium chloride was present.

In analyzing the salts chlorine was determined as silver chloride, sometimes in separate portions, in other cases in the filtrates from which thorium hydroxide had been precipitated; thorium was weighed as oxide after precipitation with ammonia, and the cæsium in the filtrates was converted into normal sulphate and weighed as such; water was determined by difference.

3 : 1 Cæsium Thorium Chloride, $3CsCl.ThCl_4.12H_2O$. — This salt was produced from solutions containing about 12 g. of thorium chloride and from 30 to 110 g. of cæsium chloride. It forms colorless crystals of feathery structure upon cooling very concentrated solutions. Three different crops made under somewhat varied conditions gave the following results upon analyses:

	Calculated for $Cs_3ThCl_7.12H_2O$.	Found.		
		I.	II.	III.
Cæsium	36.45	36.21	36.14	. . .
Thorium . . .	21.20	20.70	21.68	21.05
Chlorine . . .	22.61	23.09	. . .	23.37
Water	19.74	(20.00)	. . .	. . .

2 : 1 Cæsium Thorium Chloride, $2CsCl.ThCl_4.11H_2O$. — This salt was obtained in colorless crystals, somewhat resembling the previous salt, but not nearly as feathery in appearance. It was formed in concentrated solutions containing about 65 g. of thorium chloride and from 30 to 100 g. of cæsium chloride. The following analyses were made of different crops:

	Calculated for $Cs_2ThCl_6.11H_2O$.	Found.			
		I.	II.	III.	IV.
Cæsium . .	29.26	29.84	29.10	28.92	. . .
Thorium . .	25.52	25.42	25.41	25.70	25.22
Chlorine . .	23.43	23.40	24.75	23.35	23.55
Water . .	21.78	(21.34)	(20.74)	(22.03)	. . .

The salt loses water slowly in the desiccator over sulphuric acid. A sample dried in this way lost six per cent in two days, eleven per cent after one week, and twenty per cent, corresponding to practically all the water, after one month.

The two chlorides that we have obtained are different in type from the potassium salt $KCl.2ThCl_4.18H_2O$ described by Cleve,* and from the ammonium salt $8NH_4Cl.ThCl_4.8H_2O$ described by Chydenius.† It seems certain that the ammonium salt just mentioned represents a mixture for it is described as a sintered mass made in the dry way.

* Bulletin, xxi, 118. † Pogg. Ann., cxix, 43.

ON A CÆSIUM TELLURIUM FLUORIDE.

By H. L. WELLS and J. M. WILLIS.

Several tellurium double fluorides have been described: $NaF.TeF_4$ by Berzelius, $KF.TeF_4$, $NH_4F.TeF_4$, and $BaF_2.2TeF_4.H_2O$ by Hogbom.* It is noticeable that all these fluorides belong to a type which is different from that of the double chlorides, bromides, and iodides of tellurium, *e. g.*, $2KCl.TeCl_4$, $2RbBr.TeBr_4$, and $2CsI.TeI_4$, etc., which have been thoroughly studied in this laboratory by Wheeler.† We have undertaken, therefore, an investigation of the combination of cæsium fluoride with tellurium fluoride, with the expectation that possibly several types of double fluorides might be obtained. After a systematic examination of the matter, however, we were able to prepare only one double fluoride, $CsF.TeF_4$, which corresponds in type to the previously known fluorides.

A concentrated solution of TeF_4 was prepared by dissolving about 10 g. of pure TeO_2 in an excess of strong hot hydrofluoric acid, and to this cæsium fluoride was added in small portions, the liquid being concentrated by evaporation and cooled after each addition. At the same time small portions of tellurium fluoride were added to a concentrated solution of about 50 g. of cæsium fluoride in hydrofluoric acid, and this solution was evaporated and cooled in the same manner. Under the widest range of conditions, however, only a single double salt was obtained.

1 : 1 Cæsium Tellurium Fluoride, $CsF.TeF_4$. — This salt crystallizes beautifully in large, transparent, colorless needles. The presence of free hydrofluoric acid is necessary for its formation, for it is decomposed by water. Several crops,

* Bulletin, xxv, 60. † Amer. Jour. Sci., III, xlv, 267.

made under widely varying conditions, were analyzed with the following results:

	Calculated for $CsTeF_5$.	Found.			
		I.	II.	III.	IV.
Cæsium . .	37.36	36.59	37.50	38.56	37.23
Tellurium . .	35.96	35.51	36.45	35.82	35.60
Fluorine . .	26.68	26.76	24.51	26.18	. . .

Fluorine was determined volumetrically by converting it into SiF_4, collecting this in water, and titrating with a standard solution of potassium hydroxide. In another portion, after evaporating with concentrated sulphuric acid, and dissolving the residue in hydrochloric acid, tellurium was precipitated with sulphur dioxide, collected on a Gooch crucible, and weighed as metal. From the filtrate from the tellurium cæsium was obtained, and weighed as normal sulphate.

SHEFFIELD SCIENTIFIC SCHOOL,
May, 1901.

GENERALIZATIONS ON DOUBLE HALOGEN SALTS.

By H. L. WELLS.

THE object of this communication is to point out some conclusions in regard to double halides in general. For this purpose a rather full list of these compounds has been prepared. This list is not supposed to be complete, for the literature has not been searched with care except in the cases of certain series which have been studied in the laboratory,* but it is believed to be sufficiently complete for the purpose in view. Care has been taken to consult the original articles where salts of unusual composition have been described, and a few of these have been discarded on account of evidence that they were not real compounds, but no double salt has been rejected simply because it appeared to be irregular.

It has been thought best to limit the present discussion to the salts of the alkali metals, ammonium, and univalent thallium; for to include the double halides of the organic bases and those in which bivalent metals form the more positive halides would greatly enlarge the list, probably without giving any additional insight into the nature of the compounds.

For the sake of convenience the double salts will be arranged according to types, which will be designated by ratios indicating the number of atoms of the two metals; thus, $KCl.SnCl_4$ is a 1 : 1 salt; $2KCl.PtCl_4$ is a 2 : 1 salt; and $CsCl.2PbCl_2$ is a 1 : 2 salt. The number referring to the atoms of alkali metal, etc., will be invariably placed first.

* See Amer. Jour. Sci. from 1892 to the present time. References are given beyond to most of these articles, but reference to general literature is not attempted.

I. Salts of Univalent Negative Metals.

*Cuprous Salts.**

3 : 1	2 : 1	3 : 2	1 : 1
$3CsCl.CuCl.H_2O$	$2NH_4Cl.CuCl$	$3CsCl.2CuCl$	$NH_4Cl.CuCl$
	$2NH_4Br.CuBr$		$NH_4Br.CuBr$
	$2KCl.CuCl$		$NH_4I.CuI.H_2O$
2 : 3	1 : 2		
$2NH_4Cl.3CuCl$	$CsCl.2CuCl$		

Silver and Aurous Salts.†

2 : 1	1 : 1
2KI.AgI	$NH_4Cl.AgCl$
2RbI.AgI	KCl.AgCl
2CsCl.AgCl	KI.AgI
	KCl.AuCl

II. Salts of Bivalent Negative Metals.

Beryllium Salts.

2 : 1	1 : 1
$2KF.BeF_2$	$KF.BeF_2$
$2KCl.BeCl_2$	

Magnesium Salts.‡

1 : 1

$NH_4Cl.MgCl_2.6H_2O$	$KCl.MgCl_2.6H_2O$
$NH_4Br.MgBr_2.6H_2O$	$KBr.MgBr_2.6H_2O$
$NH_4I.MgI_2.6H_2O$	$KI.MgI_2.6H_2O$
$NaF.MgF_2$	$RbCl.MgCl_2.6H_2O$
$NaCl.MgCl_2.H_2O$	$CsCl.MgCl_2.6H_2O$
	$CsBr.MgBr_2.6H_2O$

* See Amer. Jour. Sci., III, xlvii, 96.

† See Ibid., xliv, 155.

‡ See Wells and Campbell, Ibid., III, xlvi, 431.

*Manganese Salts.**

2 : 1	1 : 1
$2NH_4Cl.MnCl_2.2H_2O$	$NH_4Cl.MnCl_2.2H_2O$
$2RbCl.MnCl_2.2H_2O$	$KCl.MnCl_2.2H_2O$
$2CsCl.MnCl_2.2H_2O$	$CsCl.MnCl_2.2H_2O$

Ferrous and Nickel Salts.

2 : 1	1 : 1
$2NH_4Cl.FeCl_2$	$KF.FeF_2.H_2O$
$2KF.FeF_2$	$NH_4Cl.NiCl_2.6H_2O$
$2KCl.FeCl_2.2H_2O$	$NaF.NiF_2.H_2O$
$2NH_4F.NiF_2.2H_2O$	$KF.NiF_2.H_2O$
$2KF.NiF_2$	$CsCl.NiCl_2$
	$CsBr.NiBr_2$

Cobalt Salts.†

3 : 1	2 : 1	1 : 1
$3CsCl.CoCl_2$	$2NH_4F.CoF_2.2H_2O$	$NH_4Cl.CoCl_2.6H_2O$
$3CsBr.CoBr_2$	$2CsCl.CoCl_2$	$NaF.CoF_2.H_2O$
	$2CsBr.CoBr_2$	$KF.CoF_2.H_2O$
	$2CsI.CoI_2$	$CsCl.CoCl_2.2H_2O$

Cupric Salts.‡

2 : 1	3 : 2	1 : 1
$2NH_4F.CuF_2.2H_2O$	$3CsCl.2CuCl_2.2H_2O$	$NH_4F.CuF_2.2\frac{1}{2}H_2O$
$2NH_4Cl.CuCl_2.2H_2O$		$NH_4Cl.CuCl_2.2H_2O$
$2NH_4Br.CuBr_2.2H_2O$		$LiCl.CuCl_2.2H_2O$
$2KF.CuF_2$		$KF.CuF_2$
$2KCl.CuCl_2$		$RbF.CuF_2$
$2CsCl.CuCl_2$		$CsCl.CuCl_2$
$2CsCl.CuCl_2.2H_2O$		$CsBr.CuBr_2$
$2CsBr.CuBr_2$		

* See Saunders, Amer. Chem. Jour., xiv, 152.
† See Campbell, Amer. Jour. Sci., III, xlviii, 418.
‡ See Wells and Dupee, Ibid., III, xlvii, 91.

*Zinc Salts.**

4 : 1	3 : 1	2 : 1
$4NH_4Cl.ZnCl_2$	$3NH_4Cl.ZnCl_2$	$2NH_4F.ZnF_2.2H_2O$
	$3CsCl.ZnCl_2$	$2NH_4Cl.ZnCl_2$
1 : 1	$3CsBr.ZnBr_2$	$2NH_4Cl.ZnCl_2.H_2O$
$NH_4Cl.ZnCl_2.2H_2O$	$3CsI.ZnI_2$	$2NH_4Br.ZnBr_2$
$NaF.ZnF_2$		$2NH_4I.ZnI_2$
$NaI.ZnI_2.3H_2O$		$2NaCl.ZnCl_2.3H_2O$
$KF.ZnF_2$		$2NaI.ZnI_2.3H_2O$
$KI.ZnI_2$		$2KF.ZnF_2$
		$2KCl.ZnCl_2$
		$2KI.ZnI_2$
		$2CsCl.ZnCl_2$
		$2CsBr.ZnBr_2$
		$2CsI.ZnI_2$

Cadmium Salts.†

4 : 1	3 : 1	2 : 1
$4NH_4Cl.CdCl_2$	$3CsBr.CdBr_2$	$2NH_4Cl.CdCl_2$
$4NH_4Br.CdBr_2$	$3CsI.CdI_2$	$2NH_4Cl.CdCl_2.H_2O$
$4KCl.CdCl_2$		$2NH_4Br.CdBr_2.\frac{1}{2}H_2O$
$4KBr.CdBr_2$		$2NH_4I.CdI_2.2H_2O$
		$2NaCl.CdCl_2.3H_2O$
1 : 1		$2NaBr.CdBr_2.5H_2O$
$NH_4F.CdF_2$		$2NaI.CdI_2.6H_2O$
$NH_4Br.CdBr_2.\frac{1}{2}H_2O$		$2KCl.CdCl_2$
$NaBr.CdBr_2.2\frac{1}{2}H_2O$		$2KCl.CdCl_2.H_2O$
$KCl.CdCl_2$		$2KBr.CdBr_2$
$KCl.CdCl_2.\frac{1}{2}H_2O$		$2KI.CdI_2.2H_2O$
$KBr.CdBr_2.\frac{1}{2}H_2O$		$2CsCl.CdCl_2$
$KI.CdI_2.H_2O$		$2CsBr.CdBr_2$
$CsCl.CdCl_2$		$2CsI.CdI_2$
$CsBr.CdBr_2$		
$CsI.CdI_2$		

* See Wells and Campbell, Amer. Jour. Sci., III, xlvi, 431.

† See Wells and Walden, Ibid., 425.

Stannous Salts.

4 : 1	2 : 1	1 : 1
$4NH_4Cl.SnCl_2.3H_2O$	$2NH_4F.SnF_2.2H_2O$	$NH_4I.SnI_2$
$4KCl.SnCl_2.3H_2O$	$2NH_4Cl.SnCl_2.H_2O$	$NH_4I.SnI_2.1\frac{1}{2}H_2O$
		$NaI.SnI_2$
2 : 3		$KI.SnI_2.1\frac{1}{2}H_2O$
$2NaF.3SnF_2$		
$2KF.3SnF_2.H_2O$		

*Mercuric Salts.**

3 : 1	2 : 1	1 : 1
$3CsCl.HgCl_2$	$2NH_4Cl.HgCl_2.H_2O$	$NH_4Cl.HgCl_2$
$3CsBr.HgBr_2$	$2NH_4Br.HgBr_2$	$NH_4Cl.HgCl_2.H_2O$
$3CsI.HgI_2$	$2NH_4I.HgI_2.3H_2O$	$NH_4Br.HgBr_2$
	$2NaCl.HgCl_2$	$NH_4I.HgI_2.H_2O$
	$2NaI.HgI_2$	$LiCl.HgCl_2$
	$2KCl.HgCl_2.H_2O$	$NaCl.HgCl_2.1\frac{1}{2}H_2O$
	$2KBr.HgBr_2$	$NaBr.HgBr_2$
	$2KI.HgI_2$	$NaI.HgI_2.1\frac{1}{2}H_2O$
	$2RbCl.HgCl_2$	$KCl.HgCl_2$
	$2RbCl.HgCl_2.2H_2O$	$KCl.HgCl_2.H_2O$
	$2CsCl.HgCl_2$	$KBr.HgBr_2$
	$2CsBr.HgBr_2$	$KBr.HgBr_2.H_2O$
	$2CsI.HgI_2$	$KI.HgI_2.1\frac{1}{2}H_2O$
		$RbCl.HgCl_2$
		$CsCl.HgCl_2$
		$CsBr.HgBr_2$
		$CsI.HgI_2$
		$TlCl.HgCl_2$

2 : 3	1 : 2	1 : 5
$2NH_4Cl.3HgCl_2.4H_2O$	$KCl.2HgCl_2.2H_2O$	$NH_4Cl.5HgCl_2$
$2CsI.3HgI_2$	$RbCl.2HgCl_2$	$CsCl.5HgCl_2$
	$CsCl.2HgCl_2$	
	$CsBr.2HgBr_2$	
	$CsI.2HgI_2$	

* See Amer. Jour. Sci., III, xliv, 221.

Palladious, Platinous, and Iridious Salts.

2 : 1		1 : 1
$2NH_4Cl.PdCl_2$	$2KCl.PdCl_2$	$LiCl.PtCl_2.6H_2O$
$2NH_4Cl.PtCl_2$	$2KCl.PtCl_2$	$KCl.PdCl_2$
$2NH_4I.IrI_2$	$2KBr.PtBr_2$	$KCl.PtCl_2$
$2NaCl.PdCl_2$	$2CsCl.PdCl_2$	$RbCl.PtCl_2$
$2NaCl.PtCl_2.4H_2O$	$2CsCl.PtCl_2$	

*Lead Salts.**

4 : 1	2 : 1	1 : 1
$4CsCl.PbCl_2$	$2NH_4Br.PbBr_2.H_2O$	$NH_4Cl.PbCl_2.\frac{1}{3}H_2O$
$4CsBr.PbBr_2$	$2KBr.PbBr_2.H_2O$	$NH_4I.PbI_2.2H_2O$
	$2RbCl.PbCl_2.\frac{1}{2}H_2O$	$KCl.PbCl_2.\frac{1}{3}H_2O$
1 : 2	$2RbBr.PbBr_2.\frac{1}{2}H_2O$	$KBr.PbBr_2.\frac{1}{3}H_2O$
$NH_4Cl.2PbCl_2$		$KBr.PbBr_2.H_2O$
$NH_4Br.2PbBr_2$		$KI.PbI_2.2H_2O$
$KCl.2PbCl_2$		$RbI.PbI_2.2H_2O$
$KBr.2PbBr_2$		$CsCl.PbCl_2$
$RbCl.2PbCl_2$		$CsBr.PbBr_2$
$RbBr.2PbBr_2$		$CsI.PbI_2$
$CsCl.2PbCl_2$		
$CsBr.2PbBr_2$		

III. Salts of Trivalent Negative Metals.

Aluminum Salts.

3 : 1	2 : 1	3 : 2	1 : 1
$3NH_4F.AlF_3$	$2NaF.AlF_3$	$3NaF.2AlF_3$†	$NaCl.AlCl_3$
$3NaF.AlF_3$	$2KF.AlF_3$		$KCl.AlCl_3$
$3KF.AlF_3$			$KBr.AlBr_3$
			$KI.AlI_3$

Vanadium Salts.

3 : 1	5 : 2	2 : 1
$3NH_4F.VF_3$	$5NaF.2VF_3.H_2O$	$2NH_4F.VF_3.H_2O$
		$2KF.VF_3.H_2O$
1 : 1		
$NH_4F.VF_3.2H_2O$		

* Nearly all the older work on double halides of lead was entirely erroneous. See Remsen and Herty, Amer. Chem. Jour., xiv, 107; Wells, Amer. Jour. Sci., III, xlv, 121; Wells and Johnson, Ibid., xlvi, 25, 34.

† The formula for chiolite is somewhat doubtful. Some authorities prefer the formula $5NaF.3AlF_3$, but the simpler formula is selected here.

*Chromium Salts.**

3 : 1	2 : 1	1 : 1
$3NH_4F.CrF_3$	$2NH_4F.CrF_3.H_2O$	$KCl.CrCl_3$
$3KF.CrF_3$	$2NH_4Cl.CrCl_3.H_2O$	
$3KCl.CrCl_3$	$2NaF.CrF_3.H_2O$	
$3TlCl.CrCl_3$	$2KF.CrF_3.H_2O$	
	$2KCl.CrCl_3.2H_2O$	
	$2CsCl.CrCl_3.H_2O$	
	$2CsCl.CrCl_3.4H_2O$	

Titanous and Manganic Salts.

3 : 1	2 : 1
$3NH_4F.TiF_3$	$2NH_4F.MnF_3$
	$2NaF.MnF_3$
	$2KF.MnF_3$
	$2NH_4F.TiF_3$

Ferric Salts.†

3 : 1	2 : 1	1 : 1
$3NH_4F.FeF_3$	$2NH_4F.FeF_3$	$NH_4Br.FeBr_3.2H_2O$
$3KF.FeF_3$	$2NH_4Cl.FeCl_3$	$CsCl.FeCl_3$
$3CsCl.FeCl_3.H_2O$	$2NaF.FeF_3.\frac{1}{2}H_2O$	$CsBr.FeBr_3$
$3TlCl.FeCl_3$	$2NaCl.FeCl_3.H_2O$	
	$2KF.FeF_3$	
	$2KCl.FeCl_3.H_2O$	
	$2RbCl.FeCl_3H_2O$	
	$2RbBr.FeBr_3.H_2O$	
	$2CsCl.FeCl_3.H_2O$	
	$2CsBr.FeBr_3.H_2O$	

Arsenious Salts.‡

3 : 2	
$3RbCl.2AsCl_3$	$3CsCl.2AsCl_3$
$3RbBr.2AsBr_3$	$3CsBr.2AsBr_3$
$3RbI.2AsI_3$	$3CsI.2AsI_3$

* See Wells and Boltwood, Amer. Jour. Sci., III, i, 249.
† See Walden, Ibid., III, xlviii, 283.
‡ Wheeler, Ibid., III, xlvi, 88.

Indium Salts.

3 : 1	2 : 1
$3KCl.InCl_3.1\frac{1}{2}H_2O$	$2NH_4Cl.InCl_3.H_2O$

*Antimonious Salts.**

4 : 1	3 : 1	7 : 3
$4NH_4I.SbI_3.3H_2O$	$3NH_4Cl.SbCl_3.1\frac{1}{2}H_2O$	$7KCl.3SbCl_3$
	$3NaF.SbF_3$	$7KBr.3SbBr_3.8H_2O$
	$3NaCl.SbCl_3$	$7RbCl.3SbCl_3$
		$7RbBr.3SbBr_3$

2 : 1	3 : 2	1 : 1
$2NH_4F.SbF_3$	$3NH_4I.2SbI_3.3H_2O$	$NH_4Cl.SbCl_3$
$2NH_4Cl.SbCl_3$	$3NaI.2SbI_3.12H_2O$	$NH_4I.SbI_3.2H_2O$
$2NH_4Cl.SbCl_3.H_2O$	$3KI.SbI_3.3H_2O$	$KF.SbF_3$
$2LiF.SbF_3$	$3RbCl.2SbCl_3$	$KI.SbI_3.H_2O$
$2KF.SbF_3$	$3RbBr.2SbBr_3$	$RbCl.SbCl_3$
$2KCl.SbCl_3$	$3RbI.2SbI_3$	$CsF.SbF_3$
$2KCl.SbCl_3.2H_2O$	$3CsCl.2SbCl_3$	
$2CsF.SbF_3$	$3CsI.2SbI_3$	

3 : 4	4 : 7	1 : 2
$3NH_4I.4SbI_3.9H_2O$	$4CsF.7SbF_3$	$RbCl.2SbCl_3$
		$CsF.2SbF_3$

1 : 3

$CsF.3SbF_3$

Auric Salts.†

1 : 1

$NH_4Cl.AuCl_3.H_2O$	$KIAuI_3$
$NH_4Cl.AuCl_3.2\frac{1}{2}H_2O$	$RbCl.AuCl_3$
$NaCl.AuCl_3.2H_2O$	$RbBr.AuCl_3$
$NaBr.AuBr_3.2H_2O$	$CsCl.AuCl_3$
$KCl.AuCl_3.\frac{1}{2}H_2O$	$CsCl.AuCl_3.\frac{1}{2}H_2O$
$KCl.AuCl_3.2H_2O$	$CsBr.AuBr_3$
$KBr.Aubr_3.2H_2O$	$TlCl.AuCl_3$

* See Wheeler, Amer. Jour. Sci., III, lxvi, 269; Wells and Metzger, Ibid., June, 1901.

† See Wells and Wheeler, Ibid., III, xliv, 157.

Bismuth Salts.

4 : 1

$4NH_4Cl.BiCl_3$

$4KI.BiI_3$

2 : 1

$2NH_4Cl.BiCl_3$

$2NaCl.BiCl_3.3H_2O$

$2KCl.BiCl_3.2H_2O$

$2KI.BiI_3.H_2O$

1 : 2

$NH_4Cl.2BiCl_3$.

3 : 1

$3NH_4Cl.BiCl_3$

$3NaCl.BiCl_3$

$3KCl.BiCl_3$

$3KI.BiCl_3$

$3RbCl.BiCl_3$

$3CsCl.BiCl_3$

3 : 2

$3NaI.2BiI_3$

$3KCl.2BiCl_3$

$3CsCl.2BiCl_3$

7 · 3

$7RbCl.3BiCl_3$

1 : 1

$NH_4Cl.BiCl_3$

$KCl.BiCl_3.H_2O$

$KI.BiI_3$

$RbCl.BiCl_3.H_2O$

*Thallic Salts.**

5 : 1

$5TlI.TlI_3$

3 : 2

$3KCl.2TlCl_3.1\frac{1}{2}H_2O$

$3LBr.2TlBr_3.3H_2O$

$3KI.2TlI_3.3H_2O$

$3CsCl.2TlCl_3$

$3CsBr.2TlBr_3$

3 : 1

$3NH_4Cl.TlCl_3.2H_2O$.

$3NH_4Cl.TlCl_3$

$3NH_4I.TlI_3$

$3LiCl.TlCl_3.8H_2O$

$3NaCl.TlCl_3.12H_2O$

$3KCl.TlCl_3.2H_2O$

$3RbCl.TlCl_3.H_2O$

$3RbBr.TlBr_3.H_2O$

$3CsCl.TlCl_3.H_2O$

$3TlCl.TlCl_3$

$3TlBr.TlBr_3$

2 : 1

$2KCl.TlCl_3.2H_2O$

$2RbCl.TlCl_3.H_2O$

$2CsCl.TlCl_3$

$2CsCl.TlCl_3.H_2O$

1 : 1

$NH_4Br.TlBr_3.2H_2O$

$NH_4Br.TlBr_3.4H_2O$

$NH_4Br.TlBr_3$

$NH_4I.TlI_3$

$KBr.TlBr_3$

$KI.TlI_3$

$RbBr.TlBr_3$

$RbI.TlI_3$

$CsBr.TlBr_3$

$CsI.TlI_3$

$TlCl.TlCl_3$

$TlBr.TlBr_3$

* See Pratt, Amer. Jour. Sci., III, xlix, 397.

Rhodium, Ruthenium, Iridium, and Osmium Salts.

3 : 1		2 : 1
$3NH_4Cl.RhCl_3.1\frac{1}{2}H_2O$	$3NaBr.IrBr_3.\frac{1}{2}H_2O$	$2NH_4Cl.RhCl_3.H_2O$
$3NH_4Cl.IrCl_3.1\frac{1}{2}H_2O$	$3KCl.RhCl_3$	$2NH_4Cl.RuCl_3$
$3NH_4Br.IrBr_3.\frac{1}{2}H_2O$	$3KCl.IrCl_3.3H_2O$	$2NH_4Cl.OsCl_3.1\frac{1}{2}H_2O$
$3NH_4I.IrI_3.\frac{1}{2}H_2O$	$3KBr.IrBr_3.3H_2O$	$2KCl.RhCl_3.H_2O$
$3NaCl.RhCl_3.9H_2O$	$3KI.IrI_3$	$2KCl.RhCl_3.3H_2O$
$3NaCl.IrCl_3.12H_2O$	$3KCl.OsCl_3.6H_2O$	$2KCl.RuCl_3$

IV. Salts of Quadrivalent Negative Metals.

Titanic, Germanium, and Manganese Salts.*

2 : 1	
$2NH_4F.TiF_4$	$2RbF.TiF_4$
$2NaF.TiF_4$	$2KF.MnF_4$
$2KF.TiF_4.H_2O$	$2KF.GeF_4$

Zirconium Salts.†

4 : 1	3 : 1	5 : 2	2 : 1
$4LiF.ZrF_4.\frac{2}{3}H_2O$	$3NH_4F.ZrF_4$	$5NaF.2ZrF_4$	$2NH_4F.ZrF_4$
	$3KF.ZrF_4$		$2LiF.ZrF_4$
			$2NaF.ZrF_4$
			$2NaCl.ZrCl_4$
			$2KF.ZrF_4$
			$2CsF.ZrF_4$

5 : 3	1 : 1	2 : 3
$5TlF.3ZrF_4$	$KF.ZrF_4.H_2O$	$2CsF.3ZrF_4.2H_2O$
	$CsF.ZrF_4$	
	$TlF.ZrF_4$	
	$TlF.ZrF_4.H_2O$	

* Rose's compounds, $6NH_4Cl.TiCl_4$ and $3NH_4Cl.TiCl_4$ are omitted here because they represent sublimates of variable composition. Pennington's salt $4CsF.TiF_4$ is also left out, as it was described with two other cæsium salts of very suspicious composition which are referred to under the pentivalent compounds.

† See Wells and Foote, Amer. Jour. Sci., IV, i, 18; iii, 466.

Stannic and Antimony Salts.

4 : 1	2 : 1	
$4NH_4F.SnF_4$	$2NH_4Cl.SnCl_4$	$2KF.SnF_4.H_2O$
	$2LiF.SnF_4.2H_2O$	$2KCl.SnCl_4$
	$2NaF.SnF_4$	$2RbCl.SnCl_4$
	$2NaCl.SnCl_4$	$2CsCl.SnCl_4$
	$2NaCl.SnCl_4.6H_2O$	$2CsCl.SbCl_4$
	$2NaBr.SnBr_4.6H_2O$	

*Tellurium Salts.**

2 : 1		1 : 1
$2KCl.TeCl_4$	$2RbI.TeI_4$	$NH_4F.TeF_4$
$2KBr.TeBr_4.2H_2O$	$2CsCl.TeCl_4$	$KF.TeF_4$
$2KI.TeI_4.2H_2O$	$2CsBr.TeBr_4$	$CsF.TeF_4$
$2RbCl.TeCl_4$	$2CsI.TeI_4$	
$2RbBr.TeBr_4$		

Ceric Salt.

3 : 2

$3KF.CeF_4.2H_2O$

Platinum Group Salts.

2 : 1		
$2NH_4Cl.PdCl_4$	$2NaCl.IrCl_4.6H_2O$	$2KCl.OsCl_4$
$2NH_4Cl.RuCl_4$	$2NaCl.OsCl_4$	$2KBr.PdBr_4$
$2NH_4Cl.IrCl_4$	$2NaBr.IrBr_4$	$2KBr.PtBr_4$
$2NH_4Cl.PtCl_4$	$2NaI.PtI_4.6H_2O$	$2KBr.IrBr_4$
$2NH_4Cl.OsCl_4$	$2NaI.IrI_4$	$2KI.PtI_4$
$2NH_4Br.PtBr_4$	$2KCl.PdCl_4$	$2KI.IrI_4$
$2NH_4Br.IrBr_4$	$2KCl.RuCl_4$	$2RbCl.PtCl_4$
$2NH_4I.PtI_4$	$2KCl.PtCl_4$	$2CsCl.PtCl_4$
$2LiCl.PtCl_4.6H_2O$	$2KCl.IrCl_4$	$2TlCl.PtCl_4$
$2NaCl.PtCl_4.6H_2O$		

* See Wheeler, Amer. Jour. Sci., III, xlv, 267.

*Plumbic Salts.**

2 : 1

$2NH_4Cl.PbCl_4$	$2RbCl.PbCl_4$
$2KCl.PbCl_4$	$2CsCl.PbCl_4$

Thorium Salts.†

3 : 1	2 : 1
$3CsCl.ThCl_4.12H_2O$	$2KF.ThF_4.4H_2O$
	$2CsCl.ThCl_4.11H_2O$

1 : 1	1 : 2
$KF.ThF_4.\frac{1}{2}H_2O$	$KCl.2ThCl_4.18H_2O$

V. Salts of Quinquivalent Negative Metals.‡

4 : 1	2 : 1	1 : 1
$4NH_4Cl.SbCl_5$	$2KF.AsF_5$	$KF.AsF_5$
	$2NH_4F.SbF_5$	$NH_4F.SbF_5$
	$2KF.SbF_5$	$NaF.SbF_5$
	$2KF.NbF_5$	$KF.SbF_5$
	$2RbF.NbF_5$	
	$2NH_4F.TaF_5$	
	$2NaF.TaF_5$	
	$2KF.TaF_5$	
	$2RbF.TaF_5$	

* See Amer. Jour. Sci., III, xlvi, 180.

† The salt $8NH_4Cl.ThCl_4.8H_2O$, described by Chydenius as a sintered mass is rejected, as is also $8KF.7ThF_4.6H_2O$, which Chydenius himself considered to be probably a mixture.

‡ Pennington's salts, $7CsF.NbF_5$ and $15CsF.TaF_5$ are omitted because they differ entirely from two rubidium salts obtained in the same investigation (which are given in the list), and because they depend upon single partial analyses. (See Jour. Amer. Chem. Soc., xviii, 59.) It is impossible to believe that cæsium and rubidium salts of the same metals should differ so widely as they appear to do.

Types arranged according to the Valency of the Negative Metals.

In this table the number of salts given in the preceding lists is placed under each type.

																Total.
I.	...	...	3:1 1	...	...	2:1 6	3:2 1	...	1:1 7	...	2:3 1	...	1:2 1	...	...	17
II.	...	4:1 9	3:1 12	...	...	2:1 80	3:2 1	...	1:1 83	...	2:3 4	...	1:2 13	...	1:5 2	204
III.	5:1 1	4:1 3	3:1 45	5:2 1	7:3 5	2:1 46	3:2 23	...	1:1 45	3:4 1	...	4:7 1	1:2 3	1:3 1	...	175
IV.	...	4:1 2	3:1 3	5:2 1	...	2:1 68	3:2 1	5:3 1	1:1 8	...	2:3 1	...	1:2 1	...	...	86
V.	...	4:1 1	...	...	...	2:1 9	...	...	1:1 4	...	...	...	...	...	...	14
Total.	5:1 1	4:1 15	3:1 61	5:2 2	7:3 5	2:1 209	3:2 26	5:3 1	1:1 147	3:4 1	2:3 6	4:7 1	1:2 18	1:3 1	1:5 2	496

Upon examining this table a marked similarity is to be noticed in the different series; the 2:1 and 1:1 types are common to all; the 4 : 1, 3 : 1, 3 : 2, and 1 : 2 types are found in all but one; while 2 : 3 types are found in three of the series. Besides the seven types just mentioned there are eight others, but only one of the latter exists in more than one series, and most of them are represented by only a single salt. It is quite possible that some of these unusual ratios are due to erroneous descriptions of salts, but it is certain that many of them represent real compounds.

The remarkable similarity in the prominent types of the series of different valencies leads to the conclusion that *the valency of a negative halide has no influence upon the types of double salts that it forms.* For, if valency had an influence, it would be expected that the five series would show marked differences from one another, and probably the halides of higher valency would tend to combine with a larger number of alkaline halide molecules. Instead of progression of types as valency increases, however, the tables show a marked symmetry in types, and their arithmetical limits in both directions are as nearly constant as could be expected considering the variations in the numbers of known salts in the different series. The prominence of the 3:1 and 3:2 types in the trivalent series may perhaps be taken as an indication that the rule is not absolute, but since these types are not the only prominent ones, and since both of them occur in three other series, the circumstance that many are found in the trivalent series may be accidental.

The facts, mentioned above, that the ratios of the different series are nearly symmetrical and that the arithmetical limits of the types in *both directions* are nearly uniform appear to be important, for they indicate that the ratios according to which positive and negative halides combine are not influenced to any great degree by the positive or negative nature of the halides. In other words, *the molecules of alkaline halides possess nearly the same combining power as molecules of negative halides.* Perhaps this point may be made clearer by the state-

ment that if all the ratios in the table are read backward they remain almost unchanged in their arithmetical aspect, and in the cases of most of the prominent ratios there is actually no change; for instance, the list of ratios 5 : 1, 3 : 1, 2 : 1, 3 : 2, 1 : 1, 2 : 3, 1 : 2, 1 : 3 and 1 : 5 is the same whether read forward or backward, and to these ratios belong almost 95 per cent of the salts here considered. It is evident, however, that positive and negative halides are not of *exactly* equal numerical importance, for to the left of the 1 : 1 ratio in the table, toward the positive halide end, the ratios are more numerous and the salts far more abundant than toward the negative halide end; it appears to be the 3 : 2 ratio column that forms a nearly symmetrical dividing line between the positive and negative ends, and even with this division the salts on the positive side predominate in number.

Another point to which attention may be called is that *salts of simple types predominate.* More than 71 per cent of the salts in the list belong to the 2 : 1 and 1 : 1 ratios, while the 4 : 1, 3 : 1, 3 : 2, 2 : 3, and 1 : 2 ratios represent over 25 per cent of them. The remaining eight types, most of which are more complex, include less than three per cent of all the salts. The fact that the 2 : 1 and 1 : 1 ratios are so important in *all* the series is another indication that valency does not influence the ratios according to which halides combine. Another evidence of simplicity is the circumstance that as far as is known not more than five molecules of one halide can combine with one molecule of another in extreme cases, while the usual limit is 2, 3, or 4. It is undoubtedly a fact that there are a few complicated salts which are not derived from mixtures or poor analyses. For example, the antimony salts to which is here given the 7 : 3 ratio have been thoroughly investigated, and without doubt possess either this ratio or one still more complex.

The conclusions that have been reached above are not encouraging in the way of giving an insight to the structure of double halides, for, if valency plays no part in this, the number of halogen atoms likewise has no influence, and such

laws or rules, based on halogen atoms, as have been advanced must be abandoned. Professor Remsen's law,* which states that the number of alkaline halide molecules that can combine with a negative halide molecule is not greater than the valency of the latter, is one of these. The stepped line in the table of ratios shows a region in the upper left-hand corner which is beyond the domain of this law. At the time that the law was brought forward it seemed reasonable, for there were only two or three possible exceptions to it. With our present knowledge of the subject, however, it is evident that it is an accidental circumstance that the law applies to so many double halides, for it is the small number of known double halides of univalent negative metals, as well as the rarity of salts of high alkali-metal ratios in the subsequent series, which determines the comparatively small number of exceptions to this rule. Werner's theory,† depending as it does upon definite numbers of halogen and other atoms, appears to have no application to the double halides in general. Possibly it may apply to the salts that form complex ions in solution.

A prevalent idea concerning the influence of valency in the formation of simple oxygen salts seems to need revision also, for halogen and oxygen salts appear to be governed by the same laws. For instance, there is no good reason for considering the valency of sulphur to have an influence upon the types of sulphates that can exist, and consequently for imagining an ideal or " ortho " sulphate such as K_6SO_6.

As far as double oxygen salts are concerned, there can be little doubt that they are analogous to double halogen salts. Their molecules usually unite in 2 : 1 or 1 : 1 ratios. A double oxygen salt, however, in view of the analogy between double halogen and simple oxygen salts, may be considered as analogous to a double-double halogen salt, if such there be. Possibly some of the complex types of double halogen salts may be due to such combinations; for instance, $2Rb_3SbCl_6$ (unknown) $+ RbSbCl_4 = 7RbCl.3SbCl_3$.

* Amer. Chem. Jour., xi, 296; xiv, 85.

† Zeitschr. anorg. Chem., iii, 267.

The stability of double halogen salts when they are dissolved in water varies exceedingly, but since gradations occur, and there is no sharp dividing line between classes of different stability, it cannot be supposed that there is any real difference in structure, as far as the solid state is concerned, between these different classes. In fact, salts that are isomorphous and evidently strictly analogous vary greatly in their behavior in solution; for example, the octahedral salts K_2PtCl_6, K_2SnCl_6, and K_2PbCl_6. Although only two classes of double salts, based on their behavior in solution, are usually recognized, there are three more or less distinctly defined groups. The first, of which K_8PtCl_6 is an example, undergo ionization into alkali-metal ions and complex negative ions with little or no decomposition into the simple halides. It is this class which displays a striking similarity to simple oxygen salts. They are comparatively few in number, but the double cyanides, which are probably entirely analogous to double halides, furnish many examples of them. The second group consists of salts that readily separate into their component halides in solution, but which may be recrystallized unchanged from water or from dilute acid solutions. To the third class belong salts that require the presence of an excess of one of their halides in solution in order that they may be formed. Sometimes the excess required is very great, so that the proportion of halides in the solution is widely different from that in the salt that crystallizes out. It is by varying the proportions of two halides greatly that a series of several double salts may sometimes be produced from them.

The fact that the same two halides may unite in several proportions to form different double salts is a point that has been sometimes disregarded by chemists. Some investigators have been content with the preparation of a single compound in cases where several might have been produced. This is a matter that should be borne in mind in the study of the physical properties of solutions. The largest number of double halides that have been produced by combining two simple halides appears to be five; for instance, five cæsium mercuric

chlorides and five cæsium antimonious fluorides, are the most extensive series of this kind that are known. Such series appear to be limited by a sort of overlapping of conditions; for compounds that are expected from analogy, intermediate between two that are produced, often cannot be prepared, and where a single double salt is very stable it may be the only one that can be made. Where several double halides of the same two simple halides exist, it is usually the case that one of them is the most stable one, and that this is produced by the recrystallization of the others, but cases occur where two of the salts, at least, are unchanged by recrystallizing.

The water of crystallization of double halides appears to present precisely the same problem as in the case of simple salts, for we find double salts of the same type possessing no water and varying quantities of it, and no good evidence is to be found that in these compounds a molecule of water is equivalent to an alkaline halide molecule, a relation similar to that, for example, that has been supposed to exist between the compounds $FeSO_4.7H_2O$ and $FeSO_4.(NH_4)_2SO_4.6H_2O$.

It has been pointed out previously * that double halides seem to show an increase in stability and variety from the iodides to the chlorides, and apparently also to the fluorides. It is probable that this is a general rule among these compounds.

It has been shown † also that with the metals magnesium, zinc, cadmium, and mercury the tendency to form double halides increases with the atomic weights. This tendency is found in other cases also, but from a comparison of the zirconium and thorium salts, as well as the antimonious and bismuth salts, it seems doubtful that this is a rule that applies in all cases.

It has been found in some cases ‡ that cæsium appears to form more extensive series of double salts than the other alkali-metals, but evidently there are exceptions to this rule, for Wells and Campbell § were unable to prepare any cæsium magnesium iodide, although both ammonium and potassium magnesium iodides are known.

* Amer. Jour. Sci., III, xlvi, 431.
† Ibid., xlvi, 434.
‡ Ibid., III, xlvi, 223.
§ Ibid., 432.

The rule advanced by Godeffroy * that all the double salts of cæsium are less soluble than those of the other alkali metals, while true in most instances, is apparently not invariable, for Wells and Campbell † found that the 1 : 1 cæsium-zinc salts, if they exist at all, are too soluble to be crystallized in a satisfactory condition, although corresponding ammonium and potassium salts are known.

Professor Remsen ‡ has called attention to the fact that certain double halides show gradations in water of crystallization, increasing with the atomic weight of the halogen and decreasing with the atomic weight of the alkali metal. An inspection of the lists of salts shows that there are many instances of analogous salts to which these rules apply, particularly in the larger amounts of water in sodium and lithium salts and in iodides, and the smaller amounts of water in cæsium salts and in fluorides; but, taking the list as a whole, these gradations are not very striking, and there are a few apparent exceptions to them.

It has been noticed in some cases that cæsium halides combine with a greater number of negative halide molecules than do other alkaline halides, while at the other end of a series more molecules of a lighter alkaline halide than of a cæsium halide may combine with a negative halide. For instance, the cæsium-zirconium and potassium-zirconium fluorides § show this relation in the following ratios of their salts:

$CsF : ZrF_4$		2 : 1	1 : 1	2 : 3
$KF : ZrF_4$ . . .	3 : 1	2 : 1	1 : 1	. . .

This is evidently not a general rule, however, for there is a 1 : 5 ammonium-mercuric chloride corresponding to the extreme type of cæsium-mercuric chlorides, while at the positive end the cæsium-lead and cæsium-mercuric salts extend farther than the salts of other alkali metals.

* Berichte, ix, 1365. † Amer. Jour Sci., III, xlvi, 434.
‡ Amer. Chem. Jour., xiv, 88.
§ Wells and Foote, Amer. Jour. Sci., IV, i, 18.

Many irregularities appear in the list. Sometimes fluorides, chlorides, bromides, and iodides seem to be analogous, but often they are not. There are some curious relations of this sort. For instance, all the double fluorides of tellurium are 1 : 1 salts, while the other tellurium salts belong to the 2 : 1 type; there is only one chloride among twelve 1 : 1 thallic salts, while all the 2 : 1 salts and nearly all the 3 : 1 salts are chlorides.

Perhaps the most marked case of uniformity in double halides is the invariability of the 2 : 1 type in the salts of the quadrivalent platinum group metals, and this type predominates to a remarkable extent among the salts of the other quadrivalent elements. There are several other well-marked groups, such as the 1 : 1 magnesium salts with six molecules of water, the 2 : 1 chromium and ferric salts with one water, and the 3 : 2 anhydrous arsenious, antimonious, and bismuth salts.

It may be stated that in our study of double halides about one-third of the compounds given in the list have been prepared in this laboratory. Some indications of regularity have been observed in connection with these researches, but it must be admitted that the results have been negative as far as throwing light upon the structure of this class of compounds is concerned.

Summary. — In the present discussion, by the method of comparison, the most important conclusion appears to be that the valency of negative halides has little or no influence upon the types of double halides that they form.

It has been shown also that the combining power of negative halides, whatever their valency may be, is nearly the same as that of alkaline halides.

Attention has been called to the prominence of simple types among these double salts.

It has been pointed out that double halides probably increase in ease of formation and variety from the iodides to the fluorides; but that other gradations and analogies which exist in some cases are probably not general.

The classification of double halides into three groups based upon their behavior in solution has been advocated: (1) Salts that form complex ions. (2) Other salts that can be recrystallized from water or dilute acids. (3) Salts that require the presence of an excess of one of their components for their formation.

SHEFFIELD SCIENTIFIC SCHOOL,
May, 1901.



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